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THE CRYSTAL STRUCTURE OF ANHYDROUS SILICOTUNGSTIC ACID[1] AND RELATED COMPOUNDS, AND THEIR PROBABLE MOLECULAR FORMULAS

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Silicotungstic acid crystallizes in a number of forms with different amounts of water of hydration. It occurs as octahedrons with the following composition, $2H_2O.SiO_2.12WO_3.30H_2O$ and as rhombohedrons, $2H_2O.SiO_2.12WO_3.24H_2O$. An isomeric triclinic form with 22 molecules of water of hydration has been described, and also one containing 17 molecules of water of hydration, but the anhydrous acid obtained by heating the hydrated forms to a temperature of 220°, is obtained as a fine powder and its crystal structure has not been satisfactorily determined by optical means.

The arrangement of the atoms in the molecule has been the subject of speculation by Rosenheim, Asch and Asch, and others,[3] but the evidence offered has not been conclusive in any case.

The aim of the present research was to make an x-ray diffraction analysis of the crystal structure of silicotungstic acid and to combine these results with chemical data in an attempt to deduce the correct molecular structure, and to compare these results with previously suggested structures.

1. *Investigation of the Structure of the Acid.*—A. Chemical Examination. In this part of the work, the classical method of degrading the molecule and isolating and identifying the decomposition products was applied to silicotungstic acid. The acid was decomposed by an excess of KOH which causes the splitting off of molecules of K_2WO_4. These could be detected since they gave a yellow to white precipitate of WO_3, in the presence of strong mineral acids. The amount of acid necessary to cause the splitting of the acid molecule was established experimentally as follows: a series of solutions were prepared containing a known amount of acid, and a volume of KOH solution equal to 8, 9, 10, 11, 12, or 14 equivalents of alkali was added; after hydrolysis had reached an equi-

librium, the solutions were tested for K_2WO_4 by the addition of concentrated hydrochloric acid.

No precipitate could be obtained after the addition of 8, 9 or 10 equivalents of alkali, but one formed slowly in the solution to which 11 equivalents had been added, and an immediate precipitate was obtained from the solution containing 12 equivalents of base. These results indicated that the molecule of silicotungstic acid was split only when 11 or more equivalents of base were added, and proved experimentally that it was possible to prepare a salt containing eight basic equivalents without decomposing the acid, a possibility denied by Brauer and Flürscheim.[4]

The amount of WO_3 formed could not be determined exactly since it is not quantitatively precipitated under these conditions, but by filtering off the precipitate and extracting with ether and hydrochloric acid, various modified silicotungstic acids could be obtained. In general, very limited amounts of these acids were prepared in a pure state, but determinations of the neutral equivalent (N. E.) and the percentage of anhydride gave the following results.

	ANHYDRIDE	N. E.
A. After adding 14 equivalents of alkali:		
Experimental values (average)	95.01%	616
Theory for $2H_2O.SiO_2.10WO_3.5H_2O$	94.96	627
B. After adding 18 equivalents:		
Experimental values	94.67%	502
Theory for $2H_2O.SiO_2.8WO_3.4H_2O$	94.65	506
C. After adding 20 equivalents:		
Experimental values	95.22%	595
Theory for $3H_2O.(SiO_2.7WO_3)_2.4H_2O$	94.90	591

The formulas given correspond to the composition of the acids when dried at 100°. Acid A is well known as silicodecitungstic acid, and is regularly prepared by boiling silicotungstic acid with a slight excess of ammonia, and recrystallizing the barium salts. Acid B, silicoöctatungstic acid, and acid C, silicoheptatungstic acid, have not been previously described as decomposition products, though Rosenheim[5] has reported a salt of the latter prepared by synthetic methods. It was not found possible to isolate an acid with less than 7 atoms of tungsten when using the same methods. The decomposition products, therefore, indicate a comparatively stable molecular nucleus containing at least seven tungsten atoms, and the probability that the splitting off of the sixth tungsten atom causes a complete disintegration of the molecule.

B. X-ray Examination. An analysis of the acid dried at 100° using the powder method on a General Electric Diffraction Apparatus showed that silicotungstic acid, $4H_2O.SiO_2.12WO_3.4H_2O$, crystallizes as a body-centered cube. Lines corresponding to the following interplanar dis-

tances were measured with spectrograms of pure NaCl and tungsten wire as calibration. (See Plate 1.)

PLANE	$(h_2 + k_2 + l_2)$	INTERPLANAR DISTANCE	INTENSITY	LOG. a_0
211	6	4.90	5	1.07927
110_2	8	4.32	8	1.08720
310	10	3.90	6	1.09106
111_2	12	3.52	10	1.08613
321	14	3.20	1	1.07881
100_4	16	3.04	4	1.08493
110_2, 411	18	2.88	2	1.08702
210_2	20	2.72	1	1.08508
332	22	2.58	9	1.08283
211_2	24	2.48	1	1.08445
431, 501	26	2.38	5	1.08406
	28			
521	30	2.22	5	1.08491
110_4	32	2.15	1	1.08501
530	34	2.08	less than 1	1.08380
100_6	36	2.02	less than 1	1.08350
532, 611	38	1.97	3	1.08434
310_2	40	1.92	2	1.08433
541	42	1.87	2	1.08343
311_2	44	1.83	less than 1	1.08417
631	46	missing		
111_4	48	missing		
110_6, 543	50	1.72	8	1.08611
320_2	52	1.68	1	1.08331
100_8	64	1.53	8	1.08492

The weighted mean value for the side of the unit cube is log. a_0 = 1.08493 and a_0 = 12.16 A.U.

A body-centered cube of these dimensions should give two lines not obtainable when using a General Electric cassette, viz., the line corresponding to the 110 plane (d = 8.61 A.U.), and the 200 (d = 6.08 A.U.).

Their presence was verified by substituting a flat film for the regular cassette when the following values were obtained.

	Mean	Calculated
M_o-Kα line 14.75 mm. corresponding to d 8.74 M_o-Kβ line 13.2 mm. corresponding to d 8.65	8.70	8.61
M_o-Kα line 21.0 mm. corresponding to d 6.15 M_o-Kβ line 19.25 mm. corresponding to d 5.96	6.06	6.08

These values satisfied the theoretically calculated requirements, and gave 22 consecutive lines, which is considered sufficient to definitely establish the lattice structure of the acid.

Attempts to obtain the acid in the form of a crystal by dissolving the acid in anhydrous solvents failed, and it was not possible to get a unit large enough to make an examination by the Laue or Bragg methods.

PLATE I.

SPECTROGRAM OF SILICODUODECITUNGSTIC ACID $2H_2O.(6H_2O.SiO_2.12WO_3)$.

(Tungsten wire calibration)

PLATE II.

SPECTROGRAM OF SILICODUODECITUNGSTIC ACID $2H_2O.(6H_2O.SiO_2.12WO_3)$.

Six corresponding lines have been marked in each plate.

A body-centered cube may belong to space groups 197 (T^3), 199 (T^5), 204 (T_h^5), 206 (T_d^7), 209 (T_d^3), 212 (T_d^6), 217 (O^5), 220 (O^8), 229 (O_h^9), 230 (O_h^{10}),[6] but of these 206, 212, 220 and 230 require abnormal spacings not present in the lines obtained, and the symmetry requirements of space group 199 cannot be satisfied with only two molecules. The data at hand has not been sufficient to distinguish which of the remaining possibilities 197 (T^3), 204 (T_h^5), 209 (T_d^3), 217 (O^5) and 229 (O_h^9) is the particular group involved.

No spectrograms of the crystals containing 24 or 30 molecules of water of hydration have been obtained, because they effloresce rapidly in air, and do not preserve their crystal structure more than a few minutes, while an exposure of two to three days is necessary to secure a diffraction pattern when using a molybdenum target tube.

The acid when dried in air and containing somewhat more water of crystallization than the acid dried at 100°, and the latter acid containing six molecules of water of crystallization, gave the same spacings as listed in the table above. This was true also of silicodecitungstic acid and silicooctatungstic acid, which were isolated as mentioned in the previous section. The anhydride, however, gave a pattern of much lower symmetry which has not yet been interpreted.

The gravity of the anhydrous acid, $2H_2O.SiO_2.12WO_3$ calculated, from the volume of the unit cell, i.e., $(12.16 \times 10^{-8})^3$, and assuming two molecules to the cell, is 5.32, and of the acid dried at 100°, $2H_2O.SiO_2.12WO_3.6H_2O$, or $(4H_2O.SiO_2.12WO_3.4H_2O)$ is 5.52. The value obtained by pycnometric methods corresponding to the latter was 5.6.

Since the heteropoly-acids crystallize in the same system, it would be expected that dried phosphomolybdic acid would also form body-centered cubes. Examination of a sample of phosphodecimolybdic acid verified this assumption, the unit cell in this case being 14.31 A.U. on each side. The same technique for obtaining the large spacings as mentioned under silicotungstic acids was employed with similar success in this case.

2. *The Probable Formula and Structure of Silicotungstic Acid.*—In proposing a modified formula for silicotungstic acid, the following facts were considered: (1) it is very difficult to remove the so-called 4 molecules of water of hydration which are retained in the acid when it is dried at 100°; (2) there is no difference in properties or structure when the acid is dried from $2H_2O.SiO_2.12WO_3.6H_2O$ to $2H_2O.SiO_2.12WO_3$, with the loss of six molecules of water; (3) a change in the structure and in the chemical and physical properties of the acid accompanies the removal of the last two molecules of water; (4) the free acid is tetrabasic; and (5) the modified acids with 10 and 8 tungsten atoms are also tetrabasic. From this evidence it is concluded that the acid has 8 molecules of water of constitution,[7] that two of these are acidic, and that the other six are

non-acidic or alcoholic in nature, a condition found in the class of silicates known as the zeolites. The formula of the acid would be written $2H_2O\cdot(6H_2O\cdot SiO_2\cdot 12WO_3)$ or $H_4(H_{12}SiW_{12}O_{46})$ or best $H_4[(SiO_4)(W_{12}O_{30})(OH)_{12}]$.

An approximate three-dimensional conception of the molecule of silicotungstic acid may be described as follows: a central silicon atom is surrounded with four oxygen atoms to form the group SiO_4. This group forms the core of a shell of tungsten atoms which are disposed in a cube-like form. Each tungsten atom with a positive charge of six is surrounded in space by the required number of hydroxyl groups and oxygen atoms at the corners of octahedra. The four oxygens connected with silicon are shared with four of the tungsten atoms which thus have a different relationship in the structure from the other eight tungsten atoms. Each of the four unique tungsten atoms is connected with two other tungsten atoms by sharing in common an oxygen atom. The four unique tungsten atoms which are most closely related to the SiO_4 group hold the acidic hydroxyl groups which account for the tetrabasicity of the acid. Six of the remaining tungsten atoms hold one oxygen and two hydroxyl groups while sharing two other oxygens with neighboring tungsten octahedra. The final two tungsten atoms hold one oxygen instead of the two hydroxyl groups. This structure then accounts completely for the formula $H_4[(SiO_4)(W_{12}O_{30})(OH)_{12}]$.

A molecular structure of this type satisfies the following requirements indicated by chemical investigations of the acid. The linkages of all the alcoholic hydroxyl groups are the same, and are different from the linkages of the acidic hydroxyl groups. Removal of the alcoholic hydroxyl groups forms the acid $2H_2O\cdot SiO_2\cdot 12WO_3$, which is tetrabasic and essentially the same in structure as the acid $2H_2O\cdot(6H_2O\cdot SiO_2\cdot 12WO_3)$. The octabasic salts are formed by ionization and neutralization of alcoholic hydroxyl groups. In the presence of excess of alkali the outer tungstens are split off leaving salts which are derivatives of acids with less tungsten atoms, fewer hydroxyl groups, but the same basicity as listed in the previous section, viz.,

$$2H_2O\cdot(6H_2O\cdot SiO_2\cdot 12WO_3)$$
$$2H_2O\cdot(5H_2O\cdot SiO_2\cdot 10WO_3)$$
$$2H_2O\cdot(4H_2O\cdot SiO_2\cdot 8WO_3)$$

The tungsten atoms are divided into two independent sets of six each which allows the ready substitution of six molybdenum atoms for six tungsten atoms, a fact stressed by Asch and Asch. The change in structure which takes place with the formation of the anhydride can be accounted for by the regrouping of the tungsten and oxygen atoms in the central section following the removal of the acidic hydroxyl groups.

A molecular structure of this type satisfies the requirements indicated

by the x-ray investigation also. Since the unit cube of silicotungstic acid is body centered, and contains two molecules of the acid, it must have one molecule located at the center and one molecule at each corner (each of the eight corner molecules contributes one-eighth to the unit cell), in which case the limiting dimensions of the molecule itself are defined by the value

$$\frac{\sqrt{3} \times 12.16}{2} = 10.53 \text{ A.U.}$$

Goldschmidt[8] gives the diameter of the oxygen ion as 2.62 A.U. and the diameter of the hydrogen ion as 2.54 A.U., while the silicon and tungsten ions are so small that they will fit without appreciable distortion in the hollow formed by four large ions when arranged in one plane. The problem of assigning a structure to silicotungstic is therefore one of placing the large number of oxygen and hydrogen ions in a cubical arrangement, having not more than four of either along a side, since the diameter of the four ions ($4 \times 2.62 = 10.48$ A.U.) is approximately equal to the side of the molecule (10.53 A.U.).

The structure described above has a square cross-section with four large ions to the side and height of somewhat more than four ions, so that it fits the experimentally determined dimensions very closely. Examined from this point of view the long chain structure, the stereo-hexite-pentite structure of Asch and Asch[9] and Rosenheim's coördinated structure are all less satisfactory.

The model of the structure of the molecule just presented must be considered only as a working plan rather than a unique delineation, although it alone accounts satisfactorily for the chemical data and such x-ray results as may be deduced from powder diffraction patterns. Efforts are being continued to the end of preparing single crystals of this acid as well as those for the highly hydrated acid. Only by means of rotation diagrams would it be possible to determine uniquely the parameters involved in a highly complex structure. As to a cubical molecular structure with a central stabilizing SiO_4 group, there can be no question.

Summary.—1. By stepwise addition of alkali to the acid, the amount of alkali necessary to cause the initial decomposition of the acid has been determined, and a series of modified acids with 7, 8 and 10 tungsten atoms has been isolated.

2. X-ray examination of the acid shows that it crystallizes as a body-centered cube, with a side length of 12.16 A.U. This dimension applies to the acids with 8, 10 and 12 tungsten atoms, and to the modifications of the latter that contain two molecules of water ($2H_2O.SiO_2.12WO_3$) or eight molecules of water ($2H_2O.(6H_2O.SiO_2.12WO_3)$) but not to the

anhydride ($SiO_2.12WO_3$). Phosphodecimolybdic acid similarly forms a body-centered cube with a side length of 14.31 A.U.

3. A modified formula for the acid—$2H_2O(6H_2O.SiO_2.12WO_3)$ or $H_4[(SiO_4)(W_{12}O_{30})(OH)_{12}]$—and a new spatial structure have been deduced to correlate adequately the x-ray and chemical data.

[1] Throughout this paper the term silicotungstic acid will be understood to refer to silicoduodecitungstic acid.

[2] This communication is an abstract of a portion of a thesis submitted by Arthur G. Scroggie in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois.

[3] Rosenheim and Jaenicke, *Zeits. anorg. Chem.*, **100**, 319, 1917. Asch and Asch, *The Silicates in Chemistry and Commerce*, Van Nostrand, New York, **1911**, p. 95.

[4] See paper No. II of this series, *J. Am. Chem. Soc.* (in press).

[5] Rosenheim and Jaenicke, *Zeits. anorg. Chem.*, **101**, 242, 1918.

[6] Astbury and Yardley, *Phil. Trans. R. Soc. London*, **A224**, 221, 1924.

[7] Asch and Asch, ref. 3.

[8] Glocker, *Materialprüfung mit Röntgenstrahlen*, Springer, Berlin, **1927**, p. 274.

[9] Asch and Asch, *The Silicates in Chemistry and Commerce*, Van Nostrand, New York, **1911**, p. 281. Rosenheim and Jaenicke, *Zeit. anorg. Chem.*, **100**, 319, 1917.

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*BINARY SOLUTIONS OF CONSOLUTE LIQUIDS**

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It has long been known that the change of the partial pressure with the concentration for ideal solutions can be given accurately over the whole range of concentrations by the so-called Raoult law[1]

$$\frac{N_1}{N_1 + N_2} = \frac{p_2 - p'_2}{p_2}, \qquad \text{I}$$

where the first term is the mol fraction in the liquid phase and p_2 and p'_2 are the vapor pressure of the pure solvent and the partial pressure of the solvent in the solution, respectively.

We have found empirically that the behavior of other pairs of solutions can be represented with unexpected accuracy by the equation

$$\left(\frac{G_1/M_1}{G_2/M_2}\right)^a = \left(\frac{N_1}{N_2}\right)^a = K\,\frac{p_2 - p'_2}{p'_2}, \qquad \text{II}$$

where M_1 and M_2 are the gram-molecular weights of the two components in the vapor, while a and K are empirical constants, which are obtained

at present from the experimental data. Of course the ratio $(M_1/M_2)^a$ can be combined with the K to form a new constant if desired. The value of K varies with the units selected; but that of a is independent of the units. If a and K are each unity, equation II becomes identical with equation I and therefore equation I is merely a special case under equation II.

The units, in which the concentrations are expressed, can be adjusted so as to make K equal to unity. If S_1 and S_2 are values so adjusted, we have

$$\left(\frac{S_1}{S_2}\right)^a = \left(\frac{p_2 - p'_2}{p'_2}\right). \qquad \text{III}$$

By a simple transformation this becomes

$$\frac{S^a_1 + S^a_2}{S^a_2} = \frac{p_2}{p'_2}, \qquad \text{IV}$$

which is probably the form to be used for a thermodynamical deduction.

In tables 1 and 2 we give some data to show the validity of equation II in selected cases where at least one of the components is an associated liquid. In table 1 are the data by Dobson[2] for ethyl alcohol and water at 25°C. and in table 2 the data by Sameshima[3] for acetone and ethyl ether at 30°C. and 20°C.

TABLE 1

ETHYL ALCOHOL AND WATER AT 25°

$$0.61 \log \frac{G_{alc}}{G_w} - \log \frac{p_w - p'_w}{p'_w} = \log K_1 = 0.6670$$

$$0.55 \log \frac{G_w}{G_{alc}} - \log \frac{p_{alc} - p'_{alc}}{p_{alc}} = \log K_2 = 0.0030$$

GRAM % ALCOHOL IN LIQUID	LOG K_1 CALCD.	p' WATER FOUND, MM.	p' WATER CALCD., MM.	LOG K_2 CALCD.	p' ALCOHOL FOUND, MM.	p' ALCOHOL CALCD., MM.
0.0	....	23.75	...	....	0.0	...
12.36	0.8030	22.67	22.39	1.8034	10.50	15.1
20.51	0.6847	21.78	21.70	1.9185	16.66	19.07
28.40	0.6653	21.15	21.13	0.0035	22.27	22.26
33.90	0.6697	20.79	20.77	0.0028	24.90	24.25
39.92	0.6636	20.36	20.38	0.0260	26.85	27.3
50.46	0.6791	19.60	19.50	0.0048	30.73	30.68
56.50	0.6724	19.01	18.95	0.0160	32.16	31.73
71.09	0.6678	17.31	17.30	1.9948	36.64	36.89
78.07	0.6663	16.18	16.19	0.0037	39.53	39.51
90.12	0.4979	10.68	12.98	0.0829	47.40	45.50
100	....	0	...	....	59.01	...

The equation gives Dobson's values for the partial pressures of water

very well through 78 gram per cent of alcohol. The equation describes Sameshima's data very well over practically the whole range.

If we know the equations for acetone and methyl alcohol, and for acetone and water, for instance, we can calculate what solutions will have the same partial pressures of acetone and consequently what solutions would be in

TABLE 2

ACETONE AND ETHYL ETHER AT 30° AND AT 20°

$$0.88 \log \frac{N_{Et}}{N_{Ac}} - \log \frac{p_{Ac} - p'_{Ac}}{p'_{Ac}} = \log K$$

$$\log K_{30} = 0.17; \quad \log K_{20} = 0.20$$

MOL % ACETONE IN LIQUID	LOG K_{30} CALC.	p'_{30} FOR ACETONE FOUND MM.	CALCD. MM.	MOL % ACETONE IN LIQUID	LOG K_{20} CALC.	p'_{20} FOR ACETONE FOUND MM.	CALCD. MM.
0.0	....	0.0	...	0.0	....	0.0	...
3.87	0.1601	21.8	22.3	5.2	0.1828	19.6	20.3
13.27	0.2029	66.2	62.4	12.71	0.2012	41.8	41.7
25.09	0.2011	106.7	102.0	24.90	0.1916	70.2	71.0
34.54	0.1772	132.4	131.4	45.70	0.1706	105.2	106.8
49.58	0.1675	167.5	167.9	61.21	0.1623	126.8	127.5
65.07	0.1556	201.2	203.2	66.62	0.1677	135.2	137.9
70.47	0.1663	213.7	214.0	84.16	0.1544	160.5	162.6
83.81	0.1593	243.1	243.8	88.83	0.1946	167.9	168.1
93.37	0.2224	266.8	265.0	93.17	0.2137	174.5	174.2
95.28	0.2048	270.6	269.4	93.58	0.2103	175.0	174.8
97.99	0.1712	276.6	276.6	97.90	0.2032	181.4	181.3
100.00	....	282.7	...	99.59	0.1244	184.1	184.3
				100.00	....	185.2	...

equilibrium if methyl alcohol and alcohol water were, and could be kept, completely immiscible. If the concentration of acetone in grams per gram of methyl alcohol is G_1 and in grams per gram of water is G_2 we can deduce the equation for the distribution of acetone between methyl alcohol and water

$$G_1/G^{1.08}_2 = \text{const.}$$

In the Cornell laboratory Mr. Morton measured this distribution using a rubber membrane to keep the methyl alcohol and water apart. The experimentally found value was 1.09 as against the value of 1.08 calculated from the ratio of the exponents in the two-component systems. From this it follows that the exponent "a" in equation II is some measure of the relative polymerizations.

* This paper is part of a program now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[1] Cf. Hildebrand, *Solubility*, **24**, 59, 1924.

[2] *J. Chem. Soc.*, **27**, 2866, 1925.

[3] *J. Am. Chem. Soc.*, **40**, 1482, 1918.

A NEW EQUATION OF STATE

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So many equations of state have been proposed that it seems, at first sight, almost useless to add still another. However, many of the equations of state so far proposed are nothing more than empirical modifications of van der Waals' famous equation of state without a thorough study of the theoretical side; in fact, almost all of the modifications which have been proposed to van der Waals' equation lead to conditions at the critical point which are not realized in nature; for example, many of the equations lead to the result that, at the critical temperature and the critical pressure, the critical volume has two or more different values whereas, as yet, only one value has been experimentally realized. There are, also, other objections which can be raised against many of these equations. I propose, therefore, to make a brief study of the original van der Waals' equation and modify it only where it is in error on the theoretical (mathematical) side.

In his classical dissertation,[1] J. D. van der Waals put forward the equation of state:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad (1)$$

where P, V and T represent the pressure, volume and temperature, respectively, of the fluid; b is a volume proportional to the volume of the molecules, R is a constant and a/V^2 represents the cohesive pressure of the molecules. On expansion and rearrangement this equation becomes:

$$V^3 - \left(b + \frac{RT}{p}\right)V^2 + \frac{a}{p}V - \frac{ab}{p} = 0 \qquad (2)$$

which is of third degree in V and, therefore, has three roots, two of which may be imaginary, at any given temperature and pressure. At the critical point, the reasonable assumption is made that the three roots of this equation are equal. This supposition imposes three conditions on the equation and, to satisfy these three conditions, the equation must contain three parameters, the values of which can be determined from the imposed conditions. Apparently, van der Waals' equation satisfies this requirement since it has the three parameters, a, b and R. But, as the volume V increases indefinitely, van der Waals' equation must reduce to the simple gas law:

$$PV = RT, \qquad (3)$$

where R is a natural constant, independent of the nature of the gas. Hence, van der Waals' famous equation, in reality, contains only two parameters a, and b, and must, therefore, in general, be mathematically absurd. We can see this result more easily by writing equation (2) in the reduced state. To do this let us write:

$$\left.\begin{array}{lll} P = P_r P_c; & T = T_r T_c; & V = V_r V_c; \\ a = a_r P_c V_c^2; & b = b_r V_c; & K = \dfrac{RT_c}{P_c V_c} \end{array}\right\} \quad (4)$$

where P_c, T_c and V_c denote the values of the pressure, temperature and volume, respectively, at the critical point. Following the late Professor H. Kammerlingh Onnes, we shall call RT_c/P_cV_c or K, the critical ratio or the critical constant. As we shall see below, this critical constant is one of the most important constants connected with equations of state of the van der Waals' type. If, now, we insert the above values and divide both sides by V_c^3, equation (2) becomes:

$$V_r^3 - \left(b_r + \frac{KT_r}{P_r}\right) V_r^2 + \frac{a_r}{P_r} V_r - \frac{a_r b_r}{P_r} = 0. \quad (5)$$

Since, at the critical point, $P_r = T_r = 1$, equation (5) becomes:

$$V_r^3 - (b_r + K)V_r^2 + a_r V_r - a_r b_r = 0. \quad (6)$$

According to our hypothesis, at the critical point, all three values of V_r must have the same value, in this case, unity. Hence equation (6) must be identical with the equation:

$$(V_r - 1)^3 = 0 \quad (7)$$

i.e., with its expansion:

$$V_r^3 - 3V_r^2 + 3V_r - 1 = 0. \quad (8)$$

Hence, coefficients of like powers of V_r must be identical. If we carry through the calculations, we find:

$$a_r = 3; \qquad b_r = \frac{1}{3}; \qquad K = \frac{8}{3}. \quad (9)$$

Therefore, there is only one value of the critical constant K, namely, $^8/_3$, which satisfies the assumptions made in respect to van der Waals' equation at the critical point. As these assumptions, however, seem to be in accord with experimental evidence and as the values of K vary from 3.1 to about 5.0 but is never $^8/_3$, we are forced to the conclusion that van der Waals' equation is not true. Another point against this equation is that the experimental values of b_r vary from about 0.17 to about

0.28 but never reach the value of $^1/_3$ as demanded by his equation, although, in fact, as we shall find out below, the value of b_r, that is, the value of the ratio of the volume of the molecules to the critical volume, is a function of the critical constant K. Since, by van der Waals' equation, the values of K, a_r and b_r are the same for all substances and if the values of any two of the three variables, P_r, T_r and V_r, are the same for several substances, then, the value or values of the third variable must be the same for the several substances. This is known as the Law of Corresponding States. It is approximately true for many substances but, in general, it is far from true. The failure of this Law is due, as pointed out below, to the variability of the critical ratio K as well as to the variability of a fourth parameter which must be introduced to take care of the change of pressure due to a temperature change, when the volume is invariant.

The next advance was due, in my opinion, to Dieterici[2] who changed the term due to the cohesive pressure of the molecules from a/V^2 to a/V^n and determined what value of n would lead to b equal to one fourth of the critical volume, the mean of the experimental values for several substances. He found, on this assumption, that n must be equal to $^5/_3$. Nevertheless, Dieterici's equation, like its predecessor, contains only two parameters, a and b, and hence, in general, it must be mathematically absurd. Incidentally, Dieterici found that, as n was changed from *2* to $^5/_3$, the critical ratio K was changed from $^8/_3$ to $^{15}/_4$. As the experimental values of K vary over a wide range, it seems almost inconceivable to me that Dieterici did not regard n as variable from substance to substance in view of the fact that mathematics demands three parameters, although Dieterici seems to have overlooked this point completely.

Accordingly, the first modification that I propose to make in regard to van der Waals' equation is to change the term due to the cohesive pressure of the molecules from a/V^2 to a/V^n and to regard n as the missing third parameter which mathematical theory demands as pointed out above. Hence, our equation is:

$$\left(P + \frac{a}{V^n}\right)(V - b) = RT \qquad (10)$$

which in the reduced state is:

$$\left(P_r + \frac{a_r}{V_r^n}\right)(V_r - b_r) = KT_r \qquad (11)$$

where the variables and parameters have the same meaning as in equations (2) and (5) above, except that $a = a_r P_c V_c^n$.

As n will not be, in general, integral, we cannot solve our equation by

purely algebraic methods but are obliged to use the well-known methods of the calculus. If $f(x)$ be equal to zero, then the necessary and sufficient condition that this equation have two equal roots is that the first derivative of $f(x)$ with respect to x be equal to zero. If three roots of this equation be identical, then the necessary and sufficient conditions are that the first and the second derivatives of $f(x)$ with respect to x be equal to zero. If, in the equation: $f(x)$ equal to zero, there occurs another independent variable, y, then I shall assume, without proof, that the necessary and sufficient conditions that $f(x)$ have three equal roots in x are that the first and second derivatives of y with respect to x are equal to zero. If there occurs in this equation two or more independent variables, then we must use the partial derivatives of any one of the independent variables with respect to x.

In the case of our equation of state, in order that it may have three identical values for V_r, we must have the first and second partial derivatives of P_r or of T_r with respect to V_r equal to zero. It must be clearly understood that these are not two separate conditions but only one, for, as we shall see below, there exists a definite relationship among the three first partial derivatives. As I perfer the mathematical symbol, $\partial p/\partial V$, to the thermodynamical symbol, $(dp/dV)_T$, I shall use the former throughout this paper.

On rearrangement of our reduced equation, we obtain:

$$P_r = \frac{KT_r}{V_r - b_r} - \frac{a_r}{V^n{}_r} \tag{12}$$

On differentiating this equation twice, we have:

$$\frac{\partial P_r}{\partial V_r} = -\frac{KT_r}{(V_r - b_r)^2} + \frac{na_r}{V^{n+1}{}_r} \tag{13}$$

$$\frac{\partial^2 P_r}{\partial V_r{}^2} = \frac{2KT_r}{(V_r - b_r)^3} - \frac{n(n+1)a_r}{V^{n+2}{}_r} \tag{14}$$

Now at the critical point, the values of P_r, T_r and V_r are all unity and also the first and second partial derivatives are zero. On carrying through the calculations we find:

$$a_r = \frac{1}{b_r} = \frac{n+1}{n-1} = \frac{1}{2}\left\{ \pm (K^2+4)^{1/2} + K \right\}, \tag{15}$$

$$b_r = \frac{1}{a_r} = \frac{n-1}{n+1} = \frac{1}{2}\left\{ \pm (K^2+4)^{1/2} - K \right\}, \tag{16}$$

$$n = \frac{a_r + 1}{a_r - 1} = \frac{1 + b_r}{1 - b_r} = \frac{1}{K}\left\{ \pm (K^2+4)^{1/2} + 2 \right\}. \tag{17}$$

As a_r, b_r and n must obviously be positive, it is necessary to take the positive value of the radical. If, for purposes of calculation, we put:

$$\frac{K}{2} = \tan\theta \tag{18}$$

then:

$$a_r = \frac{1}{2}\left\{ (K^2+4)^{1/2} + K \right\} = \sec\theta + \tan\theta \tag{19}$$

$$b_r = \frac{1}{2}\left\{ (K^2+4)^{1/2} - K \right\} = \sec\theta - \tan\theta \tag{20}$$

$$n = \frac{1}{K}\left\{ (K^2+4)^{1/2} + 2 \right\} = \operatorname{cosec}\theta + \cot\theta \tag{21}$$

$$K = \frac{1-b_r^2}{b_r} = \frac{a_r^2-1}{a_r} = \frac{4n}{n^2-1}. \tag{22}$$

Hence we have made the rather remarkable discovery that a_r, b_r and n are not only interconnected by very simple relationships but are definite, single-valued functions of the critical ratio, K, which now becomes of fundamental importance in the theory of equations of state. As the experimental values of K obtained by different observers differ widely, it is hardly necessary to point out that the values of K, or what amounts to the same thing, the values of the critical temperature, critical pressure and critical volume, of a large number of substances should be redetermined with as much precision as possible.

If K be put equal to $^8/_3$, then the calculated values of a_r, b_r and n are 3, $^1/_3$ and 2, respectively, which is van der Waals' equation. If K be put equal to $^{15}/_4$, then the calculated values of a_r, b_r and n are 4, $^1/_4$ and $^5/_3$, which is Dieterici's equation. Hence, both van der Waals' and Dieterici's equations are only particular cases of a very much more general equation, namely, equation (10) above.

Besides the mathematical requirement of a third parameter, is there any other support of the generalization of van der Waals' equation? In van der Waals' time, the cohesive forces acting between molecules were regarded as gravitational in origin, whereas it is now almost certain that these forces are electrical in origin. As the number of electrons and the radii of their orbits vary from an atom of one element to an atom of another element, the forces between atoms, and therefore, also, the forces between molecules, which are functions of the number of, and the radii of the orbits of, electrons in an atom as well as the distance apart of atoms, will be dependent on the nature of the atom and hence of the molecule. So

that we should expect n as well as a_r and b_r to vary from substance to substance.

Since a_r, b_r and n are all definite single-valued functions of K, we should expect, from equation (11), that two substances, having the same value of K, will obey the Law of Corresponding states in a very exact manner whereas if the two substances have different K values, this law should not be exactly obeyed. A study of the results obtained by S. Young[3] seems to confirm these predictions. As, however, it is necessary to introduce a fourth parameter to take care of the temperature variability of the pressure at constant volume, it would be out of place to discuss this Law further here.

The values of b_r can be obtained by the extrapolation of the Cailletet-Mathias Law of Rectilinear Diameter to the absolute zero. The values so obtained are, within the limits of experimental error in the majority of cases, identical with those obtained by equation (20) from the experimental values of K. This seems to show that b_r is, in general, independent of the temperature, as the values calculated from K are true at the critical temperature, whereas those calculated by the other method are for the absolute zero. Accordingly, in this paper, I shall assume that b_r is not a temperature function.

Whether or not n is a temperature function, I am not ready to say. There are, however, strong reasons for supposing that, in equations of the van der Waals' type, a_r or a must decrease as the temperature rises. Accordingly, I shall assume that a_r is a function of the temperature but the choice of the temperature function must be more or less empirical at the present time. If, in equations of the type given by (10), which includes van der Waals' equation as a particular case, the absolute zero is approached, the term a/V^n remains finite if we regard a and n as constants, since the volume V approaches the limiting volume b; whereas the term $RT/(V - b)$ takes the indeterminate value $0/0$; in this case, we can replace the indeterminate value, by the rules of calculus, by the expression, RdT/dV, as the experimental values of dT/dV increase as the temperature decreases and become very large, if not infinite, for the liquid state at the absolute zero. Accordingly, by equation (10), for the liquid state, we should expect that as the temperature decreases, the vapor pressure should first decrease due to the increase of the factor (a/V^n), then should begin to increase due to the more rapid increase of the factor $RT/(V - b)$ and should reach very large, if not infinite, values at the absolute zero. Experiment does not, however, confirm this prediction. If the factor $RT/(V - b)$ becomes infinite at the absolute zero as we would expect by extrapolation to the absolute zero for the liquid state, since the extrapolated vapor pressure is zero, the factor (a/V^n) must become infinite and since V is finite and n has been chosen

as finite, then a must be infinite. The choice of the function must be arbitrary at the present time but an exponential function seems to have the surest foundation. Accordingly, I shall put

$$a = ce^{A/T} = a_r P_c V_c^n e^{A_r(1/T_r - 1)} \tag{23}$$

Hence, our equation becomes:

$$\left(P + \frac{ce^{A/T}}{V^n}\right)(V - b) = RT \tag{24}$$

which is equivalent to the following reduced form:

$$\left\{P_r + \frac{a_r e^{A_r(1/T_r - 1)}}{V_r^n}\right\}(V_r - b_r) = KT_r \tag{25}$$

where a_r has the same value as calculated above from the critical constant, because, at the critical point, T_r is unity and e^0 is unity.

Since a mathematical relationship exists among the three variables, P_r, T_r and V_r, then the following relationship connects the three first partial derivatives:

$$\frac{\partial P_r}{\partial T_r} \cdot \frac{\partial T_r}{\partial V_r} \cdot \frac{\partial V_r}{\partial P_r} = -1. \tag{26}$$

On rearrangement we have:

$$\frac{\partial P_r}{\partial T_r} = -\left(\frac{\partial P_r}{\partial V_r}\right) \Big/ \left(\frac{\partial T_r}{\partial V_r}\right). \tag{27}$$

At the critical point, both $\partial P_r/\partial V_r$ and $\partial T_r/\partial V_r$ are zero, so that $\partial P_r/\partial T_r$ is indeterminate. So that the only way that $\partial P_r/\partial T_r$ can be obtained is by actual measurement. Let us denote by J_c the experimental value of this quantity at the critical point. As the fluid is unstable at the critical volume below the critical temperature, the only way of obtaining J_c is at temperatures slightly above the critical point. The data on this new magnitude is, so far, very scanty and for the most part unreliable. If, however, we assume that it is known, it is possible to calculate A_r as follows:

$$J_c = \frac{\partial P_r}{\partial T_r} = \frac{K}{1 - b_r} + \frac{a_r A_r}{1} = \frac{1}{b_r}(1 + b_r + A_r) \tag{28}$$

where the values of K and a_r, in terms of b_r, are inserted in order to avoid radicals. Whence:

$$A_r = (J_c - 1)b_r - 1. \tag{29}$$

It is clearly seen that two substances will exactly obey the Law of Corresponding States when, and only when, they have the same values for both K and J_c.

More extended details of this new equation of state, which is nothing more than a generalization of van der Waals' equation, will be published elsewhere. Furthermore, I hope to treat other equations of state in a manner similar to that outlined above.

[1] Dissertation, Leyden, 1873.
[2] *Ann. Phys.*, **69**, 685, 1899; **5**, 51, 1901.
[3] *Stoichiometry*, 2nd edition, London.

THE EFFECT OF DIFFUSION AT A MOVING BOUNDARY BETWEEN TWO SOLUTIONS OF ELECTROLYTES

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In the determination of the transference number of an electrolyte by the method of moving boundaries, a sharp boundary is formed between the solution to be studied (an aqueous solution of silver nitrate, for instance) and another "indicator" solution containing an electrolyte with a common ion and an ion of lower mobility. Lithium nitrate fulfils these conditions as an indicator for silver nitrate. Such a boundary will move when a current is passed through it. From measurements on this motion the transference number T of one ion constituent of the leading solution may be computed from the formula

$$T = \frac{v}{V} \cdot \frac{F}{it} \qquad (1)$$

in which v is the volume swept through by the boundary, V the volume containing 1 gram equivalent of the electrolyte, F the faraday equivalent, i the current, and t the time. It has, however, been found necessary to have the concentration of the indicator solution adjusted so as not to be very far from the concentration given by the relation

$$C' = C\frac{T'}{T}$$

in which C and C' are the concentrations of the leading and indicator solutions and T and T' the corresponding transference numbers. In

recent years it has been shown that the method of moving boundaries is capable of high precision.

Since the plane of contact between solutions of two electrolytes is not, under usual conditions, either permanent or definite, it became of interest to see whether the movement of the boundary is affected by diffusion of one electrolyte into the solution of the other, as, for instance, the diffusion of silver nitrate into the lithium nitrate solution, and vice versa. To obtain data upon the effect of such a diffusion the experiment was made

TABLE 1

DETERMINATION OF THE TRANSFERENCE NUMBER OF 0.1 *N* SILVER NITRATE AT 25° BY THE MOVING BOUNDARY METHOD. EXPERIMENT WITH INTERRUPTIONS

READING CM.	VOLUME CC.	TIME SECONDS	VELOCITY OF BOUNDARY CC. PER SEC. $\times 10^7$	TRANSFERENCE NUMBER
1.0	0.1630	484	3368	0.4642
2.0	0.3284	965	3404	0.4691
3.0	0.4929	1449	3401	0.4689
	Current interrupted 9 minutes			
4.0	0.6603	1938	3407	0.4696
5.0	0.8248	2432	3391	0.4675
	Current interrupted 15 minutes			
6.0	0.9909	2919	3395	0.4679
7.0	1.1580	3406	3400	0.4686
	Current interrupted 30 minutes			
8.0	1.3242	3900	3395	0.4680
9.0	1.4919	4391	3396	0.4683
10.0	1.6600	4890	3395	0.4679

of stopping the motion of the boundary, by stopping the current, during the progress of a determination of the transference number of 0.1 *N* silver nitrate. Our usual arrangement for the determination of the transference number by the moving boundary method was used, with the cell,[1,2] constant current regulator,[3] and vibration-free support[2] already described. The indicator solution was 0.078 *N* lithium nitrate, found by previous experiment to be within the "adjustment range" for this determination. The experiment differed from the regular determination in that at three periods during the run the current (7 milliamperes) was cut off. The data taken during this run are given in table 1. The timing device giving the figures in the third column of the table operated only during the time that the current was on. Upon stopping the current the boundary, which had been very sharp and easy to locate, gradually faded out, and at the end of about a minute no evidence of discontinuity between the two solutions could be observed. However, upon starting the current again the boundary slowly reformed, and, after a period depending upon

the time the current was off, fully recovered its original sharpness.[4] As is shown in the table, interruptions of 9, 15 and 30 minutes were made during the run. Each interruption occurred at a graduation of the measuring tube. The boundary regained its original sharpness and was easily read at the next 1 cm. graduation, even after the half-hour interruption.

The most surprising observation from this experiment is, however, that the diffuse zone between the two solutions, which was for a time quite invisible and later only faintly visible as a boundary, moved at just the same rate as the fully formed boundary. This is shown by the values of the velocity v/t given in column 4 of table 1. These velocities are constant within the limit of error. It is evident that the diffusion zone must have been moving at this constant velocity even when invisible. The transference numbers computed from Equation 1 are given in the last column. The value of this constant obtained by averaging the results of determinations obtained from measurements of 7 cm. or over is 0.4682 which agrees closely with the value 0.4685 obtained by numerous other measurements that we have made on this constant.

In order to obtain a more definite idea of the extent of the diffusion which took place when the current was interrupted, readings were made on a boundary consisting of 0.1 N potassium permanganate as leading solution and 0.065 N potassium acetate as indicator. The motion of the sharp junction between the colored and colorless anions was interrupted for 30 minutes at a graduation of the measuring tube when the run had proceeded for some time. At the moment of interruption the boundary had the appearance of figure 1(a). During the interruption the permanganate diffused up the tube for about 3 mm. giving the appearance of figure 1(b). The diffused or mixed zone between the two solutions must therefore have been about 6 mm. thick. On restarting the current this diffusion layer gradually narrowed and at the end of 10 minutes, during which time a normal boundary would have moved 1 cm., the junction had regained its original sharpness. Here again the readings observed were exactly those which would have been obtained if the interruption had not occurred.

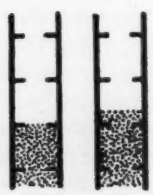

FIGURE 1

It is quite evident, therefore, that there is a powerful mechanism tending to restore a boundary to its original condition if diffusion takes place. The action of this mechanism is probably as follows. Due to the passage of current there is a drop of potential in both solutions. The potential gradient in the leading solution is, however, lower than in the following solution which contains ions of lower mobility and is also more dilute. The relations are shown diagrammatically in figure 2 in which potentials

are ordinates and distances along the measuring tube are abscissae. If, under these conditions, the relatively fast moving silver ions diffuse back into the lithium nitrate solution they encounter a high potential gradient and are rapidly sent forward to the boundary. On the other hand, if lithium ions diffuse into the silver nitrate region they move slower than the silver ions and will be finally overtaken by the moving boundary. If extensive diffusion is allowed to occur, as in the experiments described above, there will not be a sharp break in the potential as shown in figure 2, but there will be, however, a higher gradient behind any given layer of solution in the diffuse zone than there is in front. Although the presence of this restoring mechanism must have been recognized by workers in this field the only published mention of it we have found is a brief note in a paper by Denison.[5]

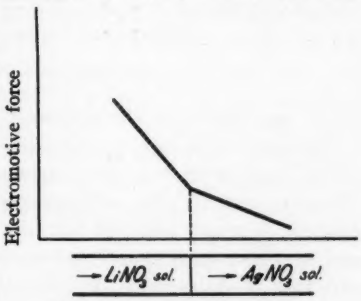

FIGURE 2.

It seems probable that the visibility of the boundary is largely determined by the change of potential gradient at that plane. Thus the silver nitrate-lithium nitrate boundary is readily observed whereas if the lithium nitrate is replaced by the corresponding sodium salt the resulting boundary is followed with the greatest difficulty. The relatively slight difference in the refractive indices of the two indicator solutions does not seem to be sufficient to account for the large difference in visibility. The difference between the potential gradients in the leading and indicator solutions is, however, cut to less than half by the substitution of sodium for lithium in the latter solution.

[1] MacInnes, D. A., and Brighton, T. B., *J. Amer. Chem. Soc.*, **47**, 994, 1925.

[2] MacInnes, D. A., Cowperthwaite, I. A., and Huang, T. C., *J. Amer. Chem. Soc.*, **49**, 1710, 1927.

[3] MacInnes, D. A., Cowperthwaite, I. A., and Blanchard, K. C., *J. Amer. Chem. Soc.*, **48**, 1909, 1926.

[4] Steele, B. D., *J. Chem. Soc.*, **79**, 423, 1901, noticed the reformation of a boundary after interruption of the current, but, in his observation "never with such clearness as in an undisturbed experiment."

[5] Denison, R. B., *Z. physik. Chem.*, **44**, 583, 1903.

ADIABATIC EXPANSION IN CASE OF VANISHING INCREMENTS

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1. *Introductory.*—The apparent possibility of reducing measurements in adiabatic expansion of gases to a ratio of successive micrometer shifts of the U-gauge interferometer seems so simple as to be worth investigating. Thus, for instance, the well-known equation of the Clement and Desormes method, in which there are 3 groups of correlative temperatures (absolute) and pressures ($\tau_1 p_1$, $\tau_2 p_2$, $\tau_3 p_3$) may be written (the subscripts denoting the direction of differences), $k/c = \Delta_{12}\log p/(\Delta_{12}\log p - \Delta_{12}\log\tau)$ if $\tau_1 p_1$ change adiabatically to τ_2 and p_2, the latter being atmospheric pressure. In the closed vessel let τ_2, p_2, change to τ_3, p_3 isometrically; then $k/c = \Delta_{12}\log p/(\Delta_{13}\log p - \Delta_{13}\log\tau)$. If now the pressure differences are all very small, so that the interferometer may be used, this equation approaches $k/c = \Delta_{12}p/(\Delta_{13}p - (p/\tau)\Delta_{13}\tau)$. Supposing that the first and final temperatures are appreciably the same so that $(p/\tau)\Delta_{13}\tau$ may be regarded as a correction $k/c = \Delta_{12}p/\Delta_{13}p$ which are the two micrometer shifts stated. The curious difficulty was encountered that the gas would not flow at a rate compatible with the experiments in question.

2. *Apparatus.*—To try this out the apparatus heretofore described was modified as shown in figure 1*a*. m,m' are the (shallow) pools of mercury of the gauge, the side v' being open to the atmosphere. The volume v communicates with the Dewar flask D, containing the sensitive thermometer T and provided with the wide stopcock C, also open to the atmosphere. The experiment begins with an exhaustion (τ_1, p_1) as indicated in the figure. C is then suddenly opened and immediately closed ($\tau_2 p_2$) so that atmospheric pressure p_2 may apparently be assumed. Thereafter with the region Dv closed, τ_3, p_3 is taken. The essential increments are $p_2 - p_1$ and $p_3 - p_1$.

As the total volume Dv was not much over half a liter (555 cm.^{3}), a clear way half-inch stopcock (length 9 cm., diameter 1.3 cm.) seemed sufficient for the transfer of air and was used.

Small increments presupposed, we may deduce from $pv = Rm\tau$ (if as before the total volume $v = Al$, A being the area of the cistern v in figure), since p varies as h, $dh/h + dh/2l = dm/m + d\tau/\tau$. Hence, the virtual pressure increment resulting from the influx of a mass dm of gas is $\Delta h = dh(1 + h/2l)$, if the change of temperature is temporarily disregarded. The corresponding increase of mass will be $dm = mdh(1/h + 1/2l) = m\Delta h/h$. If $m = 0.66$ gram, $h = 76$ cm., $l = 8$ cm., $\Delta h = 5.75\ dh$ and

$dm = 0.0505\ dh$. These constants will presently be used. The micrometer reading $r = 0.71h$.

3. *Data.*—The results obtained with this apparatus were disconcerting. Beginning with the slightly exhausted region (τ_1, p_1) it was found that suddenly opening and closing the stopcock, C, produced scarcely any change of pressure p. In fact, to increase this to atmospheric pressure p_2, it was necessary to keep the stopcock fully open more than one second. An example of the early results is given in table 1, where t denotes the time during which the stopcock was open, dh (cm. of mercury) the degree of exhaustion observed thereafter, so that $dh - dh_0$ is the observed rise of pressure due to the influx in t sec. of dm grams of air.

TABLE 1—SHOWING MASS INFLUX (dm) OF GAS IN t SEC.

t	dh	$dh - dh_0$	$\Delta h - \Delta h_0$	Δm
0 *sec.*	−0.00625 *cm.*	0.00000 *cm.*	0.0000 *cm.*	0.000000 *g.*
1	355	270	155	136
2	156	469	270	237
3	021	604	347	305

These data are reproduced in figure 1 with time (t in sec.) as the abscissa. To obtain them the day must be free from wind, since the v' end of the apparatus is open to the atmosphere, while v is closed. This means swaying fringes. Moreover, the results vary in different experiments and the volume v may be filled in 2 seconds, though never in 1 second. Mean initial rates dh/dt during the first second cluster about 0.003 cm. of Hg per sec. The exhaustion being slight the influx during the first second is about 0.00014 gram.

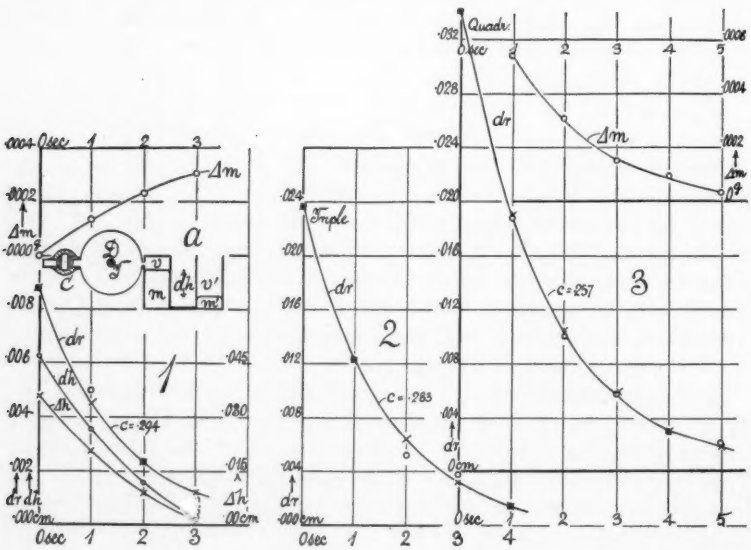
As the curve for dr is of an exponential kind, it may be replaced by the equation $dr = dr_0\ 10^{-ct}$, in which case $c = 0.294$ may be used to compute the initial results. This curve is given in figure 1 marked by crosses. Thus the micrometer reading dr would have decreased but 7%, i.e., but from 0.0089 to 0.0083 cm. if the cock C were opened and closed within $^1/_{10}$ sec.

4. *Viscosity.*—It is therefore necessary to account for this belated influx and the resistance in the stopcock first suggests itself. Since the pressure differences are kept small ($dh < 0.005$ cm. Hg) it seems not unreasonable to use the equation of viscous flow* $vp = Rm\tau = (\pi tr^4/16\eta L)(P^2_1 - p^2_1)$ neglecting surface slip. Here $r = 0.65$ cm. and $L = 9$ cm. are the radius and length of the influx pipe and P_1 and p_1 the pressures at its ends; p, v, m, τ, referring to the influx gas as above. Since $P^2 - p_1^2 = 2pdp$ very nearly, the equation may be written $dm = (\pi r^4/8\eta L)\rho t dp = C\rho t dp$ where $\eta = 0.000181$ is the viscosity, $\rho = 0.00118$ the density of the gas and $d\rho = dh\rho_m g$, if ρ_m is the density of mercury. Thus $C = 43.0$, $C\rho = 0.0508$ and $dm/dh = 677$ grams per second.

Hence, if such pressure differences dh as are given in the table were maintained, the influx of gas would be in 0–1 sec., 3.3 grams, etc., and therefore enormously out of proportion with the data for dm there inscribed. In other words, if we compute the observed successive values of the mass influx and compare these with the data obtained from the viscosity of air, the latter are over 22,000 times larger. Hence the viscous resistance of the tube is of no relevant consequence.

The same may be said of the inertia of the gas under the forces available, even if small.

The most likely explanation is to be sought in the U-gauge itself. If the cock C is opened and closed rapidly enough, the gas should cool thereafter. Hence the full equation may be taken to be $(dh/h)(1 + h/21) =$



$dm/m - (R/k)(dh/h)$, the last term being the equivalent of adiabatic $d\tau/\tau$. Numerically the equation then becomes $(dh/h)(1 + 4{,}75 + 0.289) = dm/m$. The quantity in parenthesis shows that somewhat less than 17% are to be ascribed to the observed change of head, nearly 80% to the increased volume of the gauge due to the falling head, and nearly 5% to the assumed drop of temperature. Thus the two latter causes, amounting to about 84% of the total, do not appear in the observed change of head dh. The apparatus automatically re-exhausts itself. If even more than 84% estimate is not recorded, this may be due to an accelerated fall of the gauge level.

5. *Further Experiments.*—In the preceding work the stopcock was kept open for a specified time t by the aid of a metronome beating seconds. It was found that smoother results were obtained by opening the cock for single second intervals *in succession* and observing the micrometer shift dr after each. To do this effectively, moreover, the above initial exhaustion was increased several fold. Figure 2 gives an example of this kind in which dr, the change of gauge reading ($r = 0.71h$), is taken in the course of seconds and the former exhaustion trebled. Such curves are better adapted to test the equation $dr = dr_0\, 10^{-ct}$ and the computed curves (crosses) with their extinction constants c are also given in the diagram. They show that the original exhaustion falls off $^1/_2$ in log $2/c = 1.06$ sec. and this mean rate is pretty well sustained throughout; or that the rate at which the exhaustion vanishes per sec. is proportional to the exhaustion. The rates are slower here where the cock is opened for 1 sec. successively, than when it was kept open for the corresponding number of seconds. The curve, figure 3, was obtained for an expansion four times the original value and is the best of the series when tested by the equation $dh = dh_0\, 10^{-ct}$ where $dh = 0.71dr$. The new results thus with increased precision corroborate the remarks already made above.

* O. E. Meyer, *Pogg. Ann.*, **127**, p. 269, 1866.

THE CONDITION OF SELF-OSCILLATION OF A GENERAL TRIODE SYSTEM

BY PAUL S. BAUER

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Under the hypotheses of the equivalent plate and grid circuit theorems for voltages and currents of small amplitudes,[1] it can be shown that the general equivalent circuit of a vacuum tube is that shown in figure 1, where Z_c, Z_m and Z_b are the grid-circuit, the mutual-circuit and the plate-circuit complex impedances, respectively, and μ_p, μ_g, r_p and r_g are the usual tube parameters,[2] assumed to be constant. The currents and voltages are as shown. It is proposed in this paper to develop the general relations between the circuit parameters causing the condition of self-oscillation.[3] In order that it may be quite clear what is meant by "the condition of self-oscillation," the following definition is made:

1. If we apply a complex voltage (E) to the vacuum tube circuit, shown in figure 1, at any point such that this voltage causes complex currents to flow in the various branches of the circuit, then the relation

between the circuit parameters permitting these currents to continue to flow upon removal of the voltage is defined as "the condition of self-oscillation." It has been shown[4] that an equivalent definition of "the condition of self-oscillation" is that the relation between the circuit parameters must be such that the equivalent series impedance of the vacuum tube circuit to current flow from the external voltage is zero.

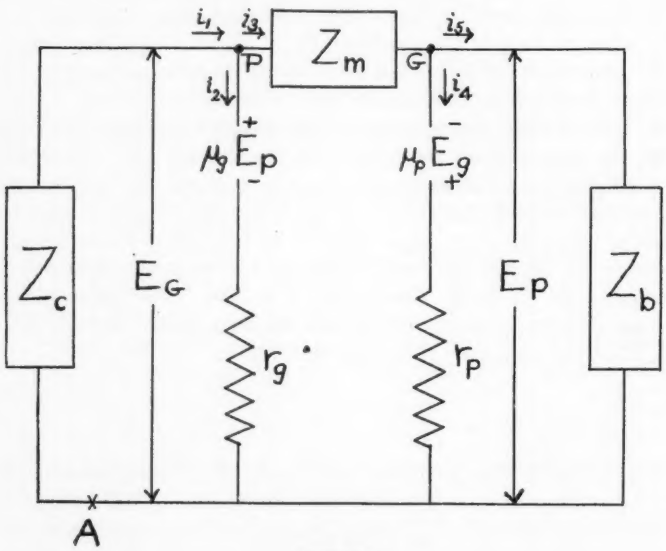

FIGURE 1

General Equivalent Circuit of a Vacuum Tube for Oscillatory Current.

2. THEOREM.—*Under the hypotheses of the equivalence theorems, the self-oscillatory relation between the circuit parameters is invariant of the point of application of the applied voltage.*

Proof.—If we apply Kirchhoff's law and the equivalence theorems to the network when the external voltage is applied at the point A, we obtain the following:

$$\begin{array}{rrrrrrr} O = & -i_1 & +i_2 & +i_3 & & & \\ O = & & & -i_3 & +i_4 & +i_5 & \\ E = & Z_c i_1 & & +Z_m i_3 & & +Z_b i_5 & \\ \mu_p E = & \mu_p Z_c i_1 & -r_g i_2 & +Z_m i_3 & +r_p i_4 & -\mu_g Z_b i_5 & (2.1) \\ -\mu_p E = & -\mu_p Z_c i_1 & & & -r_p i_4 & +Z_b i_5 & \end{array}$$

If we solve (2.1) for i_1 by Cramer's rule, we get

$$i_1 = \frac{E \begin{vmatrix} 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 & 1 \\ 1 & 0 & Z_m & 0 & Z_b \\ \mu_p & -r_g & Z_m & r_p & -\mu_g Z_b \\ -\mu_p & 0 & 0 & -r_p & Z_b \end{vmatrix}}{\Delta}, \quad \Delta \neq 0 \tag{2.2}$$

where Δ is the determinant of the coefficients of the currents.

It follows that

$$i_1 = \frac{E\Delta_1}{\Delta}, \tag{2.3}$$

where Δ_1 is the determinant whose first column consists of the coefficients of E.

In general it can be seen that if E is applied at any point in the network, the current flowing from E is given by

$$i_k = E\frac{\Delta_k}{\Delta}, \tag{2.4}$$

where k denotes the subscript of the current flowing from E.

The equivalent series impedance, Z_k, is defined by

$$Z_k = \frac{E}{i_k} = \frac{\Delta}{\Delta_k}. \tag{2.5}$$

Now Δ_k cannot be zero, since by hypothesis E is applied at a point such that i_k exists and is not equal to zero. Hence the conclusion that Z_k shall equal zero leads us to the conclusion that Δ must equal zero and Δ is invariant of the point of application of E.

THEOREM.—*A necessary and sufficient condition that the vacuum tube circuit be self-oscillatory is that the determinant of the coefficients of the equations of the currents in the system is equal to zero.*

The validity of this theorem may be at once established from the preceding proof.

3. *Evaluation of the Parametric Relationship in the General Case.*—In figure 1 the impedances are complex parameters, whose real parts may be either positive or negative quantities.

By equation (2.1), Δ is:

$$\Delta = \begin{vmatrix} -1 & +1 & +1 & 0 & 0 \\ 0 & 0 & -1 & +1 & +1 \\ Z_c & 0 & Z_m & 0 & Z_b \\ \mu_p Z_c & -r_g & Z_m & r_p & -\mu_g Z_b \\ -\mu_p Z_c & 0 & 0 & -r_p & Z_b \end{vmatrix} = 0 \tag{3.1}$$

If we reduce (3.1) by expanding in cofactors, and if we evaluate the equation of three-rowed determinants thus obtained and collect terms, we obtain by this simple algebraic process the following equation:

$$\Delta = Z_b Z_c \{[r_p(\mu_g - 1) - r_g(\mu_p + 1)] - Z_m(\mu_g\mu_p + 1)\} - Z_m(Z_c r_p + Z_b r_g) - r_p r_g(Z_b + Z_c + Z_m) = 0 \qquad (3.2)$$

This equation, by our theorem, gives us the condition of self-oscillation in our general vacuum tube circuit.

4. *Significance of the Variables in Equation* (3.2) *and the Method of Use.*—The method of using equation (3.2) to determine the frequency of self-oscillation of the triode and the relation between the inductances, capacitances, and resistances will now be explained.

The tube parameters as defined by Chaffee[2] are given below:

$$\mu_p = -\frac{\partial e_p}{\partial e_g} \qquad r_p = \frac{\partial e_p}{\partial i_p}$$
$$\mu_g = \frac{\partial e_g}{\partial e_p} \qquad r_g = \frac{\partial e_g}{\partial i_g} \qquad (4.1)$$

where e_p, e_g, i_p, i_g are the instantaneous values of the voltages on the plate and grid of the triode and the currents flowing to the plate and grid, respectively. These tube parameters are assumed constant in the neighborhood of a particular point of operation of the triode which is determined by the d.c. plate and grid voltages alone when the filament current has its rated value.

The impedances Z_b, Z_c, and Z_m are, in general, complex functions of the resistances, inductances and capacitances of the plate circuit, grid circuit and mutual circuit, and the angular velocity, ω, of the applied electromotive force.

Let L_{nh} be the hth inductance in the nth circuit, assumed constant. Let C_{nh} be the hth capacitance in the nth circuit, assumed constant. Let R_{nh} be the hth resistance in the nth circuit, assumed constant,

$$\text{where } n = b, c, m$$
$$h = 1, 2, \ldots\ldots$$

Then, on substitution of these values, the impedances Z_n can be put in the form:

$$Z_n = g_{n1}(L_{nh}, C_{nh}, R_{nh}, \omega) + jg_{n2}(L_{nh}, C_{nh}, R_{nh}, \omega), \qquad (4.2)$$

for any n, where g_{n1} and g_{n2} are real functions of real variables.

Now, substituting values of (4.2) and (4.1) for any desired circuit arrangement in equation (3.2), the latter equation will reduce to the form:

$$\Delta = f_1(L_{nh}, C_{nh}, R_{nh}, \omega) + jf_2(L_{nh}, C_{nh}, R_{nh}, \omega) = 0, \qquad (4.3)$$

$$\text{where } n = c, b, m$$

$$h = 1, 2, \ldots\ldots$$

and where f_1 and f_2 are real functions of real variables.

Equation (4.3) leads us to the following two equations, which must hold simultaneously for any values of the variables assigned:

$$\begin{aligned} f_1(L_{nh}, C_{nh}, R_{nh}, \omega) &= 0 \\ f_2(L_{nh}, C_{nh}, R_{nh}, \omega) &= 0 \end{aligned} \qquad (4.4)$$

It is thus seen that if we solve either equation for ω and substitute this value of ω in the other, both the frequency of oscillation and the relation between the circuit parameters which will cause the system to oscillate with this angular velocity may be obtained.

The author gratefully acknowledges his indebtedness to Professors E. L. Chaffee and G. W. Pierce for their helpful criticisms and suggestions.

[1] Miller, J. M., *Proc. I.R.E.*, **6**, No. 3, p. 141, 1918, and Chaffee, E. L., to be published.
[2] Chaffee, E. L., *Ibid.*, **15**, No. 3, p. 181, 1927.
[3] Hazeltine, L. A., *Ibid.*, **6**, No. 2, p. 79, 1918.
[4] Campbell, G. A., *Trans. A. I. E. E.*, **1911**.

ON THE SYMMETRY OF PROTONIC WAVE FUNCTIONS

BY BENEDICT CASSEN

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The following treatment of the symmetry properties of an H_2 molecule seem to indicate that protonic wave functions are symmetric and that, therefore, protons will satisfy the Einstein-Bose statistics.

Let p_1, e_1 be the proton and electron of a hydrogen atom a_1; p_2, e_2 those of an atom a_2. Let g_{11}, g_{12}, g_{13} be the coördinates of the center of gravity of a_1; g_{21}, g_{22}, g_{23} those of a_2. Let r_1, θ_1, ϕ_1; r_2, θ_2, ϕ_2 be, respectively, the polar coördinates of electrons e_1 and e_2, where the axis A of the polar coordinates is drawn from the center of gravity of a_1 to that of a_2 and the origin is at the center of gravity of the whole system.

The twelve coördinates g_{11}, g_{12}, g_{13}, g_{21}, g_{22}, g_{23}, r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2 completely specify the system of two protons and two electrons (except for spin coördinates). Let ψ be the wave function for the entire system.

ψ can be separated in the coördinates of the centers of gravity of the atoms and the electronic coördinates, that is

$$\psi = \psi_g \psi_e \tag{1}$$

where ψ_e is a function of r_1, θ_1, ϕ_1, r_2, θ_2, ϕ_2 and the electronic spin coordinates, while ψ_g is a function of the coördinates of the centers of gravity of the atoms and any other spin coördinates associated with them.

Considering the system as a symmetrical rotator capable of being in various rotational states, we can separate the rotational wave function ψ_R from ψ_g, that is,

$$\psi_g = \psi_R \psi_w. \tag{2}$$

ψ_R is considered as a function of ϑ and Φ, the polar angles of the axis A with respect to an axis B fixed in space. ψ_w will then involve all the coordinates, except ϑ and Φ, necessary to specify the positions of the centers of gravity of the atoms a_1 and a_2 and possible spin coördinates associated with them.

If p_1 is interchanged with p_2 and simultaneously e_1 with e_2, then this operation interchanges the centers of gravity of atoms a_1 and a_2. This has the effect of reversing the direction of the axis A so that ϑ becomes $\pi - \vartheta$ and Φ becomes $\Phi + \pi$. Then if p is the rotational quantum number, we have

$$\psi_{Rp}(p_1, e_1, p_2, e_2) = (-1)^p \psi_{Rp}(p_2, e_2, p_1, e_1) \tag{3}$$

as rotational wave functions for even p are unchanged by reversing the axis A while those for odd p are changed in sign by such a reversal. Reversing the direction of the axis A changes θ into $\pi - \theta$ and ϕ into $-\phi$. This operation leaves ψ_e unchanged when the molecule is in its lowest electronic state.

We know that the total wave function is antisymmetric in the electrons. If it is symmetric in the protons it will be changed in sign by reversing the axis A, while if it is antisymmetric in the protons it is unchanged by such a reversal. In the first case ψ_w will change its sign under the axis reversal when p is even while it will remain unchanged when p is odd and vice versa for the second case. This indicates that ψ_w does involve spin coördinates besides the vibrational wave function which latter is obviously unchanged by reversal of A. Hori's data on the band spectrum of hydrogen and Dennison's[1] theory of the rotational specific heat of hydrogen require that the relative weights of symmetric to antisymmetric rotational states should be as 1 to 3. Therefore, in case the total wave function is symmetric in the protons, the states with symmetric ψ_w should have three times the statistical weight of those with antisymmetric ψ_w and vice versa for the case when the total wave function is antisymmetric in the protons. The state of affairs is indicated in the following table.

POSSIBILITY NO.	I	II
Axial symmetry of ψ_w for odd rotational states	S	A
Symmetry of total wave function in protons	S	A
Axial symmetry of total wave functions	A	S
Axial symmetry of ψ_w for even rotational states	A	S

As a symmetric spin function has three times the statistical weight of an antisymmetrical spin function, it seems necessary to choose the first of the above alternatives requiring the total wave function to be symmetric in the protons. This result is independent of whether the protons themselves have or have not spins. The spins that give the correct relative weights to the rotational states are atomic spins pertaining to the elements of the rotator, the proton-electron pairs. Of course, it is possible that the atomic spins originate from protonic spins. If such is the case, then the coördinate function of the protons is at most antisymmetric in pairs of protons. This means physically that protons attract resonantly in groups and can repel dissonantly in pairs. If this is so it would help in the explanation of the formation of helium from protons and electrons in interstellar space as is assumed by Millikan and Cameron,[2] as the resonance forces acting between protons would tend to make their effective cross-sectional area for collision and capture large when the protons had the small velocities of the low temperatures of interstellar space.

The known information on the various isotopes of the elements show that there is a strong tendency toward what is apparently resonant pairing of nuclear electrons while no such tendency is shown for protons. This can be taken as additional evidence for resonant groupings of protons. The resonance forces between pairs of the relatively small numbers of nuclear electrons would not seem to be sufficient to stabilize the nucleus by acting against the powerful electrostatic repulsions of the protons.

If wave functions are symmetric in protons, then similar particles, atoms or molecules, containing an even number of electrons will satisfy the Einstein-Bose statistics, while those containing an odd number of electrons will satisfy the Fermi-Dirac statistics. Apparently almost all ordinary gases satisfy the Einstein-Bose statistics so that part of the van der Waal's forces in these gases will be attractive resonance forces. Probably all the van der Waal's forces for helium are of this character. According to Aston the principal isotope of xenon contains an odd number of electrons. This isotope should then show a greater vapor pressure at very low temperatures than the isotopes of even atomic weight. However, the unpaired electron is enclosed in a high potential energy wall so that equilibrium would be reached extremely slowly.

[1] *Proc. Roy. Soc.*, **1150**, 483–6, 1927.

[2] *Phys. Rev.*, **32**, 533–57, 1928.

POSITIVE ION CURRENTS IN THE POSITIVE COLUMN OF THE GLOW-DISCHARGE IN THE NOBLE GASES[1]

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The theory for the use of collectors in gas discharges, developed by Langmuir and his associates,[3] has been applied very successfully to the mercury arc. In the present experiments it was intended to study the positive column of the glow discharge in the noble gases, using Langmuir's method.[4] However, the results obtained differed markedly from those reported by Langmuir in his work on mercury vapor, and could not be interpreted on the basis of his theory.

The experiments were carried out in Ne, Ar and He, using plane collectors with a guard ring (Ni, Mg, C). The collector, placed at different distances from the wall (in most cases about 1 cm.), was insulated on the back with mica and the lead-in wires were protected by thin glass tubes. The discharge tube, diameter 6 cm., was of the normal cylindrical type with hot cathode; by changing the heating current of the filament the total current through the tube (I) could be varied within rather wide limits. Different pressures were tried, but for most of the runs the following values were taken: Ne 0.02 mm., Ar 0.01 mm., He 0.04 and 0.1 mm. The argon and helium were pure, the neon contained a few p.c. helium. Special care was taken to realize an accurate measurement of the sheath thickness.

The volt-ampere characteristic of a sounding electrode consists of three distinct parts, dependent on the potential of the collector (V_g) with respect to the space. When $V_g > 0$, the collector absorbs only electrons, for $V_g \ll 0$ the current consists of positive ions, and for voltages slightly negative both electrons and positive ions are collected. In this paper only the positive ion currents will be discussed. Langmuir,[5] and also Schottky and von Issendorff,[6] proved that for mercury the current, corresponding to $V_g \ll 0$, is due to an inflow of positive ions and not to an emission of electrons. That this current consists at least partly of positive ions was clearly shown in these experiments by the heavy sputtering of the metal, even for low accelerating potentials. In the mercury arc the positive ion part of the characteristic presents a saturation character, due to the screening of the negative charge on the electrode by the positive ion space charge. Curve (m) of figure 4, obtained in Ne ($p = 0.02$ mm.), using a plane collector (Ni) with guard ring (diam. of inner disc 10 mm.), for a total current in the tube $I = 450$ ma., shows conclusively that this is not the case in the neon discharge. Similar curves were obtained in

argon and helium. The slope of these curves is quite different from that of the Langmuir diagrams, where the current shows only a small increase due to edge corrections (which in the present case is avoided by use of a guard ring), although it is true that if these were present in the noble gases they would be much more important than in mercury.

When the electron part of the current in the transition region (where V_g is slightly negative) is plotted on semi-logarithmic paper, log i_e against V, the curve obtained is a straight line; consequently, the electrons have a velocity distribution according to Maxwell's law or at least one which is very near to it. This was always found to be the case for a very large number of runs; in many of them there was definite evidence of more than one group of electrons with different temperatures, but these data will be discussed in a subsequent paper. The electron temperatures calculated from the slope of the (logi_e, V) diagram come out very high, the highest values being found for He, the lowest for Ar. They increase with decreasing pressure and decreasing current density, the latter variation being much less pronounced than the first. Table 1 gives some data illustrating these conclusions.

TABLE 1

RUN	GAS	p	I	T_E	$\bar{V}_E$
U5H	Ne	0.02 mm.	450 ma.	53000 K.	6.85 volts
U5A	Ne	0.02	100	70000	9.05
U6D	Ar	0.01	200	24000	3.11
U6E	Ar	0.002	200	43000	5.56
U16 C15	He	0.04	600	75000	9.7
U16 C20	He	0.1	600	60000	7.77
U16 C23	He	0.1	100	68000	3.8

The space potential, derived from the kink in the semi-log diagram, was found to be for run *U5H*: $V_s = -21.5v$ with respect to the anode.

The positive space charge above the collector is visible as a dark layer whose thickness x can be measured accurately; figure 1 gives the measurements of x for run *U5H*. If the impacts of the positive ions falling through the sheath may be neglected ($x \ll \lambda$), the Child-Langmuir space charge equation $i = CV^{3/2}/x^2$ can be applied and the positive ion current, corresponding to the observed value of x_m, may be calculated. The value of V to be introduced here is the potential of the collector with respect to the space, which is obtained from the value V_a (potential with respect to the anode) plotted as abscissas in figure 1, by subtracting V_s. Curve (1) of figure 2 gives the currents computed in this way. The difference between the measured values of i_m and the calculated ones i_c amounts to one-half of i_m. We see then that $i_m > i_c$, or in another form, if from i_m we calculate the sheath thickness x_c this is found much smaller than the observed value, briefly: $x_m > x_c$.

The problem arises then how to explain these two discrepancies: the

increase of i_m with decreasing V_g and the difference between i_m and i_c, each of these effects being present in the three noble gases studied, but absent in mercury. Different possible errors were estimated but none of them was found to account for the discrepancies. One point, however, must be considered somewhat more in detail. The edge of the sheath presented a gradual transition between the dark space and the body of the discharge, looking much like the edge of a negative glow toward the cathode, and probably also due to electrons penetrating a certain distance because of their own motion. The edge of this transition region being sharper on the side of the collector, the distance from this point to the metal plate was taken for x_m, in other words, x_m as measured is too small. But correction for this would make our i_c values still smaller, and they were already found to be only about $(0.5 \times i_m)$. If the transition layer is really due to

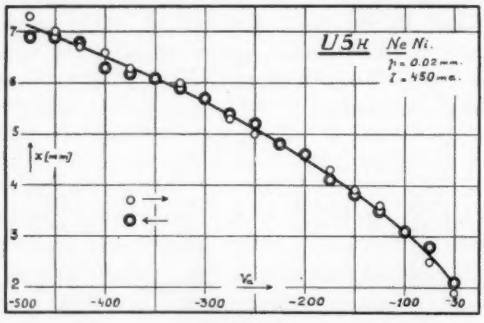

FIGURE 1

Measurement of the sheath thickness x as a function of the voltage V. Run *U5H*

the penetration of electrons into the sheath, the potential to be introduced in the space charge equation is approximately $V_a - (V_s + \overline{V}_e)$, where $\overline{V}_e$ is the average energy of the electrons; this will decrease i_c. But the ions will come into the sheath with a certain velocity, namely, the sum of $\overline{V}_e$ and V_+, the velocity they had in striking the outer edge. This will increase i_c for a given value of x_m, the measured thickness. Taking these corrections into account the difference between i_m and i_c remains about 50% of i_m. Curves (2) and (3) have been calculated with a formula derived on the assumption that the charged particles entering the sheath have a Maxwellian distribution of velocities,[7] the equivalent temperature being taken, respectively, equal to 8000° K. ($T_+ = {}^1/_7 T_-$) and 53,000° K. ($T_+ = T_-$). Thus no reasonable correction of this nature is sufficient to explain the discrepancy.

Several possible explanations suggest themselves; they are summarized below and will be briefly discussed.

1. Secondary electron emission from the metal plate, due to:
   (*a*) Normal photoelectric effect.
   (*b*) Positive ion impact.
   (*c*) Impact of metastable (*MS*) atoms.
2. Ionization in the sheath, due to:
   (*a*) Photoelectric ionization of normal atoms.
   (*b*) Photoelectric ionization of *MS* atoms.
   (*c*) Ionization by mutual impact of 2 *MS*.
   (*d*) Ionization by positive ion impact.
   (*e*) Impact-ionization by electrons liberated by one of the processes sub 1.

1*a*. Making a rough estimation of the radiation energy falling on the disk, one would have to assume a much higher efficiency for the photoelectric effect than has ever been observed.

1*b*. This possibility may be ruled out since the measurements of Penning[8] on the secondary emission due to Ne ions, give an efficiency of the order of 10%. Penning points out also that the number of secondaries per ion depends on the condition of the metal surface. The targets in his experiments stood in a fairly good vacuum, obtained by differential pumping, while in our work the metal is more likely to have an adsorbed layer of normal and excited atoms, which might increase the secondary emission.

1*c*. This effect has been observed in mercury by Webb[9] and has been studied by several of his pupils.[10] An estimation of the number of *MS* atoms that hit the collector, made by Dr. W. de Groot (unpublished), gives the right order of magnitude for the secondary emission if the efficiency of this process is assumed rather high, e.g., 50%.

2. The effects sub *a*, *b* and *c* have been discussed in an earlier paper,[11] and hypothesis *b* was found to fit the experimental data. However, a direct experimental test, performed a short time ago by Dr. W. de Groot at the Philips' Laboratory gave a negative result (unpublished). Under 2*a* would also come the ionization by *MS* atoms of sputtered metal atoms, but it is difficult to see why the effect would still be present in He, where the sputtering is almost negligible.

2*d*. This effect will probably be rather small, especially for the low accelerating potentials, because of the low efficiency of the process. Furthermore, if there were an appreciable number of impacts for the incoming ions, the sheath thickness would be decreased, and experimentally x_m was found too large.

2*e*. Since the existence of effect 1*a* and 1*b* is not open to doubt, there will always be some ionization due to electron impacts in the sheath. A rather small secondary emission could, qualitatively at least, explain the

slope of the positive ion diagram and the difference between i_m and i_c. Some of the experimental data can be understood on this basis, but with this interpretation one would expect the curve (i_m, V) to steepen with increasing pressure; experimentally the opposite was found. In fact, for rather high pressures, where the condition $(x \ll \lambda)$ is certainly no longer

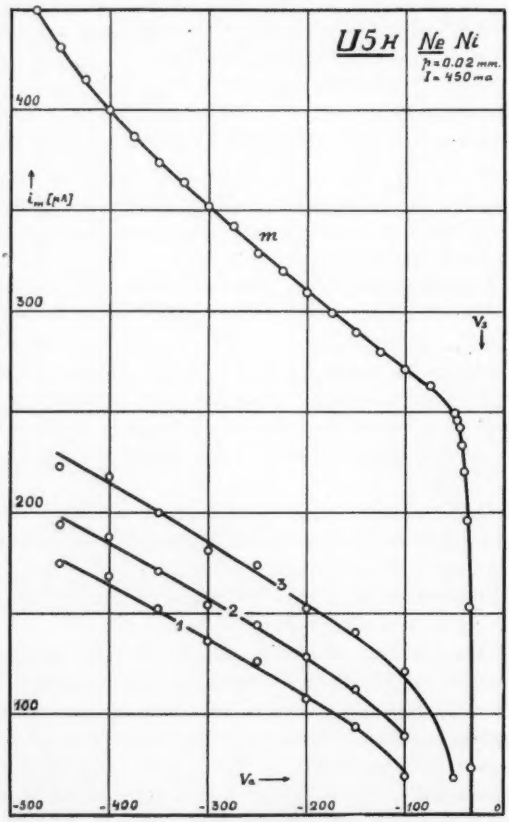

FIGURE 2

Positive ion part of the volt-ampere characteristic for run *U5H*. Curve (m): measured values; other curves: calculated from the sheath thickness x under different assumptions.

satisfied, indeed, λ was $< x$, some curves in He are parallel to the V-axis. This remarkable fact will be discussed more fully in a complete record of these experiments. So far, it has not been possible to determine definitely to which one, or ones, of the effects those discrepancies are principally due.

Finally, I want to thank Dr. G. Holst, Director of the Philips' Laboratory, and Prof. R. A. Millikan, Director of the Norman Bridge Laboratory (where the second part of this work was done), for the opportunity of working in these laboratories, Dr. W. de Groot, Dr. F. M. Penning and Prof. K. T. Compton for their interest in this work and many helpful suggestions. I acknowledge also with pleasure the considerable help given in the experimental work by Mr. J. Moubis, (Philips' Laboratory) and Mr. L. F. Green (Norman Bridge Laboratory).

[1] Preliminary abstract presented at the Berkeley Meeting (March 3, 1928) of the American Physical Society, *Phys. Rev.*, **31**, 913, 1928.

[2] Fellow in Physics of the C. R. B. Educational Foundation.

[3] Langmuir and Mott-Smith, *G. E. Rev.*, **27**, 449, etc., 1924.

[4] Those experiments were started in the spring of 1926 in the Physical Laboratory of the Philips' Glowlampworks, Eindhoven (Holland) at the suggestion of Dr. F. M. Penning.

[5] Langmuir, *Science*, **58**, 290, 1923; *G. E. Rev.*, **26**, 721, 1923.

[6] Schottky and von Issendorff, *Zeits. Phys.*, **26**, 85, 1924.

[7] Epstein, *Verh. D. Phys. Ges.*, **21**, 85, 1919; Langmuir, *Phys. Rev.*, **21**, 419, 1923.

[8] Penning, *Proc. Amsterdam Acad.*, **31**, 14, 1927; *Physica*, **8**, 13, 1928.

[9] Webb, *Phys. Rev.*, **24**, 113, 1924.

[10] Messenger, *Ibid.*, **28**, 962, 1926; Coulliette, *Ibid.*, **32**, 635, 1928.

[11] Morse and Uyterhoeven, *Ibid.*, **31**, 827, 1928. We are indebted to Dr. W. de Groot for pointing out an error in this paper in the computation of the average velocity of the ions formed in the sheath. The only effect on the final formulas, however, is a small change in the constants.

NOTE ON THE D LINE EXCITATION BY THE GREEN SODIUM BAND AND THE DISSOCIATION POTENTIAL OF SODIUM VAPOR

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The dissociation of molecules into normal and excited atoms by the absorption of light has been shown to occur in a wide variety of cases by many observers, and fluorescence and absorption experiments in which this process operates have been used to furnish values for the heats of dissociation of the molecules in question. For example, the existence of a region of continuous absorption on the short wave-length side of the ultra-violet bands of hydrogen,[1] until recently,[a] was taken as evidence for the dissociation of the hydrogen molecule into a normal and an excited atom, and the heat of dissociation calculated from this assumption was in agreement with the value obtained from an analysis of the Lyman-

Witmer[2] bands by the method of Birge and Sponer.[3] The appearance of the D lines in the fluorescent radiation, emitted when the vapor of sodium iodide is illuminated with wave-lengths shorter than 2500 Å, has been attributed by Terenin[4] to the optical dissociation of the molecule into a normal iodine atom, and a sodium atom in the $2P$ state. A third, and perhaps best known, example of such a process is the optical dissociation of iodine into a normal and metastable atom.[5] This note is a discussion of the evidence for the occurrence of such a process in the fluorescent phenomena of sodium vapor.

Years ago Wood[6] noticed, during his classical researches on sodium vapor, that the D lines were stimulated when the vapor was illuminated with light in which wave-lengths known to be absorbable by the atom were absent, and, in the last year, the experimental conditions under which the phenomenon occurred were described by Professor Wood and the author.[7] Recently the experiments have been repeated more carefully by the author, and, where before figures were only qualitative, they are now given quantitatively to within the error of measurement. A short account and discussion of the results of the work appeared in *Nature*,[8] while the method was fully described in the earlier paper.

The experiments were designed to determine the conditions under which it is possible to excite the D lines by the blue-green band of the sodium molecule. The familiar long steel tube, closed at each end with glass windows, served to enclose the shorter cylindrical steel retort, placed at its center, which contained the sodium, and in which the fluorescence occurred. An intense beam was focused in the middle of the retort through holes provided in its ends for this purpose. The beam was obtained from a large 50-ampere carbon arc, equipped with carbons impregnated with salts of the rare earths for the purpose of throwing most of the radiation into the visible region, and filtered through a monochromator of high light-gathering power. The fluorescence was observed as before by means of a right-angled prism, placed on one side of the entering beam next the glass window of the tube, whose center was heated electrically, and equipped with a thermocouple, this time, to ensure control and an even distribution of the temperature. Lead tubing coiled around the tube's ends, and carrying a rapid stream of water served to keep the waxed joints at the windows from softening.

Under this very intense illumination, the D lines appeared very distinctly in the pure fluorescing vapor, when it was illuminated with various regions in the blue-green, in which the D lines themselves were absent. But their intensity varied rather sharply with the wave-length of the exciting light, and with the temperature of the furnace. In the earlier experiments, they failed to appear in pure vapor, and were excited only when the vapor contained small quantities of a foreign gas at a pressure of

a few millimeters. The present experiments showed that a foreign gas was not at all necessary. This pressure effect was anomalous, and is seen now to be due to the way in which the intensity varies with the temperature. As pointed out previously, the atomic lines appeared somewhat below 400°, rose to a sharp maximum around 410°, and disappeared again above 450°, in the pure vapor not mixed with gas. The existence of the maximum near 410° could be detected easily. Now in the previous experiments no adequate temperature control was purposely employed, the tube being heated by bunsen burners, but it was found, in the present work, that the introduction of gas at a few millimeters pressure caused temperature changes of 10° to 20°, the temperature rising on the introduction of the gas. Experiments showed this to be due entirely to the fact that the gas reduced the diffusion of the vapor to the cooler parts of the tube. The rapidly diffusing vapor in the absence of gas keeps the heated section at a lower temperature than it would attain if this diffusion were absent. Although the *D* lines were obtained in this way in the presence of gas they were much less intense, than in the pure vapor, and appeared only in the temperature range indicated above. The existence of a temperature at which the intensity of the atomic lines excited by the green band is a maximum is caused, quite probably, by the simultaneous operation of an increasing intensity of emission, and an increasing intensity of atomic absorption, as both the molecular and atomic densities increase. The long and short wave-length limits of the exciting band, as well as the wave-length of the band which produced the maximum intensity, were measured to within 50 Å. or 0.03 volts. The following is a list of the measurements made.

1. Wave-length producing maximum *D* line fluorescence
   2.55 volts; 4856 Å.
2. Long wave-length limit of excitation of the *D* lines
   2.36 volts; 5240 Å.
3. Short wave-length limit of excitation of *D* lines
   2.76 volts; 4470 Å.
4. Wave-length producing maximum blue-green fluorescence
   2.51 volts; 4930 Å.
5. Short wave-length limit of blue-green fluorescence
   2.75 volts; 4485 Å.

It is easily seen that no such interpretation of the phenomenon, as proposed either for the case of iodine or sodium iodide, is in agreement with the energy values given above. The case analogous to iodine, for example, would be one where band fluorescence is absent on the short wave side of the long wave-length limit of the exciting light for the *D* lines. In such a case fluorescence would cease at the point where the energy was

sufficient to dissociate the molecule into a normal and 2.1-volt atom, and the atomic line would become visible. Instead, here, the band and line fluorescence exist together throughout the entire range of their excitation, and the short wave limit of excitation for both band and D line fluorescence correspond to within the error of measurement.

This correspondence between the intensity variation of the D lines and the blue-green bands is exactly what one would expect if atoms were excited to the $2P$ levels by collisions of the second kind with excited molecules. It is fairly certain now that this is the process occurring and that the excited atoms cannot arise as a result of the dissociation of the molecules. Sufficient energy for dissociation is not available. Loomis[9] gives the heat of dissociation as 1.0 ± 0.1 volt, which he obtained by extrapolating the ω_n curve for the normal level of the blue-green system by the method of Birge and Sponer. Extrapolation of the ω_n curve for the upper level gives a total energy of 3.07 volts, and assuming the products of dissociation to be a normal and 2.1 volt excited atom, the heat of dissociation, D, becomes 0.97 volts. This is a much shorter extrapolation than the first, and hence should give the more accurate value. Professor Birge, in a letter to the writer, pointed out that this gives a possible maximum value, and on replotting the ω_n curve for the upper level and giving it the negative curvature that is generally found, he finds $D = 0.84$ volts, as a possible minimum value. Very recently Polanyi and Schay[10] have determined D by what amounts to a chemical method and find it to lie between 0.71 and 0.87 volt. The extrapolated lower limit from Loomis' data as calculated by Professor Birge lies in this range so that better agreement of these values could not be expected. The value of D can be taken then as 0.85 ± 0.02 volt.

The total energy necessary for the molecule to dissociate into a normal and 2.1-volt excited atom is

$$0.85 + 2.1 = 2.95 \text{ volts}$$

and at no point in the entire range of wave-lengths which excite the D lines is this amount available. It is true that at 600°, the temperature of the experiments, the average kinetic energy is about 0.1 volt and that there will be a distribution of energy over some of the lower vibrational levels. This quantity would be available for dissociation in addition to the amount added by absorption. But when the excitation energy is 2.55 volts and the D lines have their maximum intensity, the initial energy of the molecule must be 0.4 volt to supply sufficient energy for dissociation. The number of molecules in this state will be approximately less than one two-thousandth of those in the normal state, so that the occurrence of such an absorption is highly improbable. On the other hand, it is probable that approximately three out of every ten excited molecules collide with

an atom before they radiate, so that the probability of collisions of the second kind is enormously larger than the probability of absorptions occurring which begin on an initial level of 0.4 volt.

These results emphasize the fact that in mixtures of atoms and molecules, stimulation of atomic lines by radiation which can excite only the molecule (cf. Winans, *Phys. Rev.*, **32,** 427, 1928) cannot be taken as evidence for molecular dissociation. Estimates of heats of dissociation from such experiments can be given small value.

* The experimental work was carried on while the writer was a NATIONAL RESEARCH FELLOW at Yale University.

[1] Dieke and Hopfield, *Phys. Rev.*, **30,** 400, 1927.

[2] Witmer, *Ibid.*, **28,** 1223, 1928.

[3] Birge and Sponer, *Ibid.*, **28,** 260, 1928.

[4] Terenin, *Zeit. Phys.*, **37,** 98, 1926.

[5] Dymond, *Ibid.*, **34,** 553, 1925.

[6] Wood, *Physical Optics*, p. 574.

[7] Wood and Kinsey, *Phys. Rev.*, **31,** 793, 1928.

[8] Kinsey, *Nature*, **121,** 904, 1928.

[9] F. W. Loomis, *Phys. Rev.*, **31,** 323, 1928.

[10] Polanyi and Schay, *Z. Phys. Chem.*, **1,** 30, 1928.

[6] Professor Birge has pointed out to the writer that recent plates, obtained by Professor Hopfield of the ultra-violet absorption of hydrogen, show that the region which was thought to be one of continuous absorption, turns out, under lower pressures, to consist of bands.

ON THE SUMMABILITY OF FOURIER SERIES. SECOND NOTE

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1. Shortly after our first note on the summability of Fourier series (these PROCEEDINGS, **12,** 915–918, 1928) was communicated to the Academy, we succeeded in carrying the discussion of the Hausdorff case considerably further. The present note gives a short account of the results which we have obtained in this direction. We refer to our first note for the formulation of the problem and for the notation employed.

The function $q(u)$ associated with the method (H, q) is supposed to be of bounded variation in $(0, 1)$, $q(0) = 0$ and $q(1) = 1$; further $q(u)$ must be continuous at $u = 0$ to define a regular method of summation. Let $q(u)$ be continued outside of the interval $(0, 1)$ by setting $q(u) = 0$ when $u < 0$ and $q(u) = 1$ when $u > 1$. We introduce the function

$$\Omega(h) = \operatorname*{Max}_{0<a\leqq h} \int_{-\infty}^{+\infty} \left| d[q(u + a) - q(u)] \right|, \quad h > 0, \qquad (1)$$

and consider the integral

$$\int_0^1 \frac{\Omega(h)}{h}\, dh. \tag{2}$$

THEOREM. *The Fourier series of any integrable function $f(x)$ is summable $(H, q(u))$ to the sum $f(x)$ almost everywhere if the integral* (2) *exists.*

The proof is too long to be reproduced here; the crucial point of the proof lies in showing that

$$\left| \int_0^1 (1 - u + u\, e^{it})^n\, dq(u) \right| < \text{const. } \Omega\left(\frac{\pi}{nt}\right), \tag{3}$$

when $t \geqq \pi/n$.

The existence of the integral of formula (2) evidently requires that $\Omega(h) \longrightarrow 0$ when $h \longrightarrow 0$. A sufficient condition in order that $\Omega(h)$ shall tend to zero with h is clearly that $q(u)$ is absolutely continuous, and it is very likely that this condition is also necessary.

2. It is not difficult to find examples of functions $q(u)$ for which the integral in (2) exists and which consequently give rise to methods of summation applicable to Fourier series almost everywhere. The simplest case is that mentioned in our first note in which $q'(u)$ is of bounded variation and $\Omega(h) = O(h)$. Other permissible cases are obtained by assuming $q'(u)$ to belong to a Lipschitz class; indeed, if $q'(u)$ belongs to Lip (α), $0 < \alpha \leqq 1$, then $\Omega(h) = O(h^\alpha)$. Still less restrictive is to assume that $q'(u)$ belongs to a class Lip (α, p) for some α, $0 < \alpha \leqq 1$, and some $p \geqq 1$. Logarithmic conditions of Dini's type are also in order.

The following conditions are of slightly different nature. Let $q(u)$ be convex in $(0, 1)$, $q(0) = 0$, $q(u) > 0$ when $u > 0$ and $q(1) = 1$. In this case $\Omega(h) = 2[1 - q(1 - h)]$ and condition (2) takes on a very simple form. All conditions here stated are satisfied by $q(u) = 1 - (1 - u)^k$, $k > 0$, which corresponds to the Cesàro means (C, k). Another possible choice is

$$q(u) = 1 - \left[\frac{\log a}{\log \dfrac{a}{1 - u}}\right]^\alpha, \tag{4}$$

where $a > 1$, $\alpha > 1$. The convexity condition really requires that $\log a > \alpha + 1$, but this restriction is not necessary in order that (2) shall exist since the correction in $\Omega(h)$ is merely $O(h)$. The relations of inclusion holding between these transformations and the arithmetic means are of some interest, and we are led to believe that (4) includes all Cesàro means (C, k), $k > 0$.

SUMMARY OF RESULTS AND PROOF CONCERNING FERMAT'S LAST THEOREM (THIRD PAPER)

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As in the other two papers[1] we shall divide the discussion into two cases. If in the relation

$$x^p + y^p + z^p = 0, \tag{1}$$

with x, y, z, prime to each other, xyz prime to the odd prime p, this will be referred to as case I; if one of the integers x, y, z, is divisible by p, this will be called case II. Consider Furtwängler's law of reciprocity which may be put in the form

$$\left\{\frac{\omega}{\theta}\right\}\left\{\frac{\theta}{\omega}\right\}^{-1} = \left\{\frac{\theta,\omega}{\mathfrak{p}}\right\}, \tag{2}$$

where ω and θ are any two integers in the field $k(\alpha)$ such that (ω) and (θ) are prime to each other and to $\mathfrak{p} = (1 - \alpha)$, $\alpha = e^{2i\pi/p}$. Also $[\omega/\mathfrak{q}]$ is defined as the power of α which satisfies

$$\omega^{\frac{N(\mathfrak{q})-1}{p}} = \left\{\frac{\omega}{\mathfrak{q}}\right\} \pmod{\mathfrak{q}},$$

$\mathfrak{q}$ being an ideal prime in $k(\theta)$, $N(\mathfrak{q})$ is the norm of $\mathfrak{q}$, and if $\mathfrak{Q} = \mathfrak{q}_1, \mathfrak{q}_2, \ldots \mathfrak{q}_s$, where the $\mathfrak{q}$'s are prime ideals which are prime to (ω) and $(\mathfrak{p})$, then

$$\left\{\frac{\omega}{\mathfrak{Q}}\right\} = \left\{\frac{\omega}{\mathfrak{q}_1}\right\}\left\{\frac{\omega}{\mathfrak{q}_2}\right\} \cdots \left\{\frac{\omega}{\mathfrak{q}_s}\right\}.$$

The norm residue symbol is defined by

$$\left\{\frac{\theta,\omega}{\mathfrak{p}}\right\} = \alpha^P$$

where

$$P = -l_1(\theta)\frac{N(\omega)-1}{p} + l_1(\omega)\frac{N(\theta)-1}{p} + \sum_{s=2}^{p-2}(-1)^{s-1} l^s(\theta) l^{p-s}(\omega) \tag{3}$$

and

$$l^s(\theta) = \left[\frac{d^s \log \theta(e^v)}{dv^s}\right]_{v=0}$$

and if

$$\theta = a_0 + a_1\,\alpha + a_2\,\alpha^2 + \ldots + a_{p-2}\alpha^{p-2}$$

then

$$\theta(e^v) = a_0 + a_1 e^v + a_2 e^{2v} + \ldots + e^{v(p-2)}$$

From (1) we find that the ideal $(x + \alpha y)$ is the pth power of an ideal in $k(\alpha)$, if $z \not\equiv 0 \pmod{p}$. Set $\omega = x + \alpha y$ and put $\theta = \mathfrak{q}^h$, where $\mathfrak{q}$ is a prime ideal in k, whose norm is a power of the rational prime n. Then (2) gives, since

$$\left\{\frac{\theta}{\omega}\right\} = 1 \tag{4}$$

$$\left\{\frac{\omega}{\mathfrak{q}}\right\}^h = \left\{\frac{\theta,\ x + \alpha y}{\mathfrak{p}}\right\}.$$

Consider the second case of Fermat's last theorem and let $y \equiv 0 \pmod{p}$ and assume $xyz \not\equiv 0 \pmod{\mathfrak{q}}$. Evidently for this value of ω we have

$$l^s(\omega) \equiv 0 \pmod{p},$$

$$s = 1, 2, 3, \ldots, p - 2.$$

We also have

$$\frac{N(\omega) - 1}{p} = \frac{\dfrac{x^p + y^p}{x + y}}{p} = \frac{x^p + y^p - (x + y)}{p(x + y)},$$

since it is known that if y is divisible by p it is also divisible by p^2 and also $x^p \equiv x \pmod{p^2}$ and we find

$$\frac{N(\omega) - 1}{p} \equiv 0 \pmod{p},$$

hence

$$\left\{\frac{\theta,\ x + \alpha y}{\mathfrak{p}}\right\} = 1$$

and (4) gives

$$\left\{\frac{\omega}{\mathfrak{q}}\right\}^h = 1.$$

Suppose that $\mathfrak{q}$ is selected so that $h \not\equiv 0 \pmod{p}$, then since $\mathfrak{q}$ is a prime ideal we have

$$(x + \alpha y)^c \equiv 1 \pmod{\mathfrak{q}}, \tag{5}$$

where

$$c = \frac{N(\mathfrak{q}) - 1}{p}.$$

We find similarly

$$(x + \alpha^a y)^c \equiv 1 \pmod{\mathfrak{q}} \qquad (5a)$$

for $a = 1, 2, \ldots, p-1$, and since from (1) we have $x + y = v^p$ where v is an integer, then (5) is also true for $a = 0$. Expansion gives

$$x^c + c\,\alpha^a\, x^{c-1}\, y + \binom{c}{2}\alpha^{2a}\, x^{c-2}\, y^2 + \ldots + \alpha^{ac}\, y^c \equiv 1 \pmod{\mathfrak{q}}.$$

This may be written in the form

$$A_{p-1}\,\alpha^{a(p-1)} + A_{p-2}\,\alpha^{a(p-2)} + \ldots + A_0 \equiv 0 \pmod{\mathfrak{q}},$$

where the A's are polynomials in x and y with rational integral coefficients. Letting $a = 0, 1, \ldots, p-1$ in turn we have p congruences. The determinant of the α's obtained from these congruences can be expressed aside from the powers of α as the product of factors of the type $\alpha^r - 1$, $r \not\equiv 0 \pmod{p}$ and any such expression $\not\equiv 0 \pmod{\mathfrak{q}}$. Hence

$$A_0 \equiv A_1 \equiv \ldots \equiv A_{p-1} \equiv 0 \pmod{p}.$$

Now if $s \neq 0$ then

$$\frac{A_s}{x^c} = \binom{c}{s} t^s + \binom{c}{s+p} t^{s+p} + \binom{c}{s+2p} t^{s+2p} + \ldots$$

where $y/x = t$ and

$$\frac{A_0}{x^c} + \frac{1}{x^c} = \binom{c}{o} + \binom{c}{p} t^p + \binom{c}{2p} t^{2p} + \ldots$$

Hence we have the

THEOREM: *If* (1) *is satisfied in case II with* $y \equiv 0$ (*mod* p) *then*

$$\binom{c}{s} + \binom{c}{s+p} t^p + \binom{c}{s+2p} t^{2p} + \ldots$$

is divisible by n *for* $s = 1, 2, \ldots, p-1$, *and* $y/x = t$. *Also* n *is any prime integer* $\not\equiv 0$ (*mod* p) *such that a prime ideal divisor of* n *in the field* $k(\alpha)$ *belongs to an exponent which is prime to* p, *and* $xyz \not\equiv 0$ (*mod* n).

The analogous relations in the case where none of the integers x, y, and z in (1) are divisible by p are more complicated. In this event it is convenient to select (n) to be the product of principal ideals which are primary.

In my second note under the present title already referred to I gave on page 771 Theorem D and indicated a proof. In one part of the proof it was noted that if the ideal (ω) is the pth power of an ideal in the field $k(\alpha)$ and ω is a primary number in the field, then (ω) is the pth power of the principal ideal in the same field under assumptions 1 and 2 of Theo-

rem D of that paper. It was also noted that this result could be proved independently. I shall give here this proof, which is included in the proof of a more general result in which the assumption 1 is omitted.

Consider the relation (2) and assume that

$$(\theta) = (\mathfrak{a}\,\mathfrak{a}_{-1})^g$$

where $\mathfrak{a}$ is any prime ideal in the field $k(\alpha)$ prime to ω and $\mathfrak{p}$, and $\mathfrak{a}_{-1}$ is the ideal obtained from $\mathfrak{a}$ by the substitution (α/α^{-1}), and ω is semi-primary. Further let $(\mathfrak{a}\,\mathfrak{a}^{-1})$ belong to the exponent g. By the assumption as to the second factor of the class number, g is not divisible by p. If (ω) is the pth power of an ideal in $k(\alpha)$ then

$$\left\{\frac{\theta}{\omega}\right\} = 1.$$

Hence (2) gives

$$\left\{\frac{\omega}{\theta}\right\} = \left\{\frac{\theta,\omega}{\mathfrak{p}}\right\}. \tag{6}$$

Now by definition of ω we also have[2]

$$l^s(\omega) = \left[\frac{d^s \log\,\omega}{dv^s}\right]_{v=0} \equiv 0 \pmod{p}$$

$s = 1, 2, \ldots, p-2$.

Now also

$$l^{p-1}(\omega) \equiv 0 \pmod{p}$$

(Vandiver[3]). Hence from (3) since

$$l_1(\omega) \equiv 0 \pmod{p}$$

ω being semi-primary,

$$\left\{\frac{\theta,\omega}{\mathfrak{p}}\right\} = 1,$$

and (6) gives

$$\left\{\frac{\omega}{\theta}\right\} = 1.$$

Now

$$\left\{\frac{\omega}{\theta}\right\} = \left\{\frac{\omega}{\mathfrak{a}\mathfrak{a}_{-1}}\right\}^g$$

and hence since $g \not\equiv 0 \pmod{p}$,

$$\left\{\frac{\omega}{\mathfrak{a}\mathfrak{a}_{-1}}\right\} = 1,$$

or

$$\left\{\frac{\omega}{\mathfrak{a}}\right\}\left\{\frac{\omega}{\mathfrak{a}_{-1}}\right\} = 1.$$

We have

$$\left\{\frac{\omega}{\mathfrak{a}_{-1}}\right\} = \left\{\frac{\omega_{-1}}{\mathfrak{a}}\right\}^{p-1},$$

and this yields in connection with the last relation

$$\left\{\frac{\omega\ \omega_{-1}^{p-1}}{\mathfrak{a}}\right\} = 1.$$

But by Hilbert[4] this power character must equal α^s, $s \not\equiv 0 \pmod{p}$ for an infinite number of distinct ideal primes $\mathfrak{a}$, unless $\omega\ \omega_{-1}^{p-1}$ is the pth power of an integer in $k(\alpha)$. The ideal $\mathfrak{a}$, however, is any prime which is prime to (ω) and $\mathfrak{p}$, and hence there is, at most, only a finite number of values for $\mathfrak{a}$ for which

$$\left\{\frac{\omega\ \omega_{-1}^{p-1}}{\mathfrak{a}}\right\} = \alpha^s,$$

which proves the result stated.

The above result applied to (1) gives

$$\left(\frac{x + \alpha^k y}{\alpha^k - 1}\right)\left(\frac{x + \alpha^{-k} y}{\alpha^{-k} - 1}\right)^{p-1} = \lambda^p, \tag{7}$$

where λ is an integer in $k(\alpha)$ and we assume that z is divisible by p. Using the assumption that the second factor of the class number of $k(\alpha)$ is prime to p we also have

$$\frac{(x + \alpha^k y)\,(x + \alpha^{-k} y)}{(\alpha^k - 1)\,(\alpha^{-k} - 1)} = \epsilon_k^{1}(\omega_k^{1})^p,$$

and these two relations give easily

$$\frac{x + \alpha^k y}{\alpha^k - 1} = \epsilon_k \omega^p, \tag{8}$$

where ϵ_k^{1} and ϵ_k are real units and ω is an integer in $k(\alpha)$. Also k is an integer not divisible by p.

The relation (7) may also be derived by the use of a result proved by Takagi.[5]

A simple extension of the argument on p. 770 of my second article under the present title gives the result that a unit which is congruent to a mod p^2, with a a rational integer is the pth power of a unit in $k(\alpha)$ unless there exists an integer ν in the set 1, 3, . . ., $p - 4$, such that

$$B_{\nu p} \equiv 0 \pmod{p^3}.$$

Using this result with (8) and following the argument in Kummer's 1857 memoir we may prove the following

THEOREM: *Under the assumptions*

1. *None of the Bernoulli numbers* $B_{\nu p}$, $\left(\nu = 1, 2, 3, \ldots, \frac{p-3}{2}\right)$ *is divisible by* p^2;

2. *The second factor of the class number of the field* $k(\alpha)$, $\alpha = e^{2i\pi/p}$, *is prime to* p, *then*

$$x^p + y^p + z^p = 0,$$

is not satisfied in rational integers x, y *and* z, *prime to each other, none zero, if*

$$x\,y\,z \equiv 0 \pmod{p},$$

and p *is an odd prime.*

[1] Vandiver, these PROCEEDINGS, **12**, 106–9; 767–72 (1926).
[2] Vandiver, these PROCEEDINGS, **11**, p. 294 (1925).
[3] loc. cit. pp. 294–6.
[4] Hilbert, *Jahresber. Deut. Math. Verein*, 426–8 (1897).
[5] *J. Math.*, **157**, 236 (1927).

THE DIRECT EFFECT OF TEMPERATURE CHANGES UPON THE MELANOPHORES OF THE LIZARD ANOLIS EQUESTRIS

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Introduction.—The pioneer workers in the field of color changes in animals were the first to note the effects of varying temperatures upon the condition of the reptilian melanophore. Their almost unanimous opinion was that among lacertilians the melanophores of the skin were expanded by cold and contracted by warmth; an observation since corroborated by later investigators, notably Parker (1906) working on Anolis carolinensis, and Redfield (1918) working on Phrynosoma blainvillei. These two authors agreed that above and below the critical temperatures the behavior of the melanophores was governed by the temperature of the environment rather than by the condition of illumination. The probability that the melanophores reacted directly to heat and cold was also suggested by Redfield (1918) who carried out experiments in the following way. An incision was made through the body wall of each of four horned toads, the direction of the cuts being such that if they had been performed upon

a single animal a separate piece of skin would have been removed from the body. Redfield believed that in this way he was certain of getting at least one preparation in which the melanophores of the area included by the four cuts were deprived of their nervous connections. Upon application of warmth to these areas he observed in every case a contraction of the melanophores, a reaction similar in all respects to those observed in unoperated parts of the body. He therefore concluded that the reactions of the melanophores to temperature changes were the same whether or not they were under the control of nerves. His experiments were somewhat complicated and the results were not as conclusive as could be obtained from observations on isolated pieces of reptilian skin.

Hadley (1928) has recently demonstrated an independent response to light in the melanophores of isolated skin from Anolis equestris. Upon the exposure of such a piece to direct sunlight its melanophores expanded and the skin assumed a dark brown color, but when the piece was removed to the shade its melanophores contracted and the color became a brilliant green. Owing to the certainty of these responses and the ease with which they could be reproduced the skin of this species was selected as a favorable object for the study of the direct effect of temperature changes upon the reptilian melanophore.

The skin for the following experiments was taken from lizards collected in the vicinity of Harvard House, Soledad, Cuba, where the observations were carried out. I wish to express my thanks and appreciation to Dr. Thomas Barbour for making it possible for me to avail myself of the opportunities offered by the Harvard Biological Station in Cuba and to Dr. G. H. Parker for criticism of the manuscript.

Methods.—All the experiments were performed on strips of dorsal skin averaging about 1 by 2 cm., isolated from the body of Anolis equestris. The following simple apparatus was devised for subjecting the skin to different temperatures. The strip of skin was first tied loosely at one end to a glass plate of about the same width as the strip and approximately twice as long. This support was then placed vertically in a small glass vial, the outer surface of the skin being away from the surface of the glass to which it was tied and the vial was filled with a 0.7% solution of NaCl, thus completely immersing the skin with its melanophores in a normal medium. The cork of the vial was fitted with a thermometer, whose bulb lay in close proximity to the skin. The action of heat and cold upon the melanophores could readily be determined by altering the temperature of the salt solution, this being accomplished by immersing the vial in warm or cold water. This procedure reduced to a minimum the possibility of subjecting the pigment cells to chemical or mechanical stimulation.

In the direct sunlight a bit of skin held in such an apparatus assumed a

dark brown color, but when the vial with the skin was removed to the shade the color changed to a brilliant green. By varying the position of the glass vial with reference to illumination either condition could be maintained indefinitely or altered at will. Experiments showed that the strip of skin turned green in 15 seconds and darkened in 35–40 seconds, the temperature being maintained between 29°C. and 30°C. These results agree with those obtained by Hadley (1928) and are a sufficient assurance that under the conditions of the following experiments the isolated Anolis skin responds normally to light. Prior to subjecting a strip of skin to variations in temperature, its light reactions were tested and the skin was used for experimentation only if its responses to illumination were the same as those just described. A single bit of skin was used continuously for about 30 to 40 minutes after which it was discarded.

The brilliant green color associated with removal of the excised skin to the shade is undoubtedly due to the unmasking of a layer of green chromatophores by a proximal migration of pigment granules into the central bodies of the deeper-lying melanophores. These melanophores occupy a position within the dermis but their long slender-branched processes extend well up into the layer of green pigment cells to form there an extensive and complicated network. Consequently the distal migration of the pigment of the melanophores into these processes obscures the green layer and the lizard or piece of skin from the lizard assumes a dark brown color. The withdrawal of the pigment from the processes once more exposes the green chromatophores and the lizard's skin now becomes green. It is probable, though not at present certain, that the color changes are due entirely to the activity of the melanophores, the other chromatophores playing a more or less passive rôle. For the sake of convenience the distal migration of the melanophoric pigment producing the brown color in the skin is still spoken of as an "expansion" and the reverse process, causing the change to green as a "contraction," though these terms do not imply any necessary change in the shape of the pigment cell itself.

Experimental.—Prior to each of the experiments a determination was made of the responses to light of the excised piece of Anolis equestris skin upon which the observations were to be made and if these responses agreed with those described by Hadley (1928), its melanophores were assumed to be reacting normally to illumination. The purpose of my experiments was then to discover to what extent these reactions to illumination were dependent on the temperature and with this in mind I first set about to ascertain at how high a temperature the dark brown color assumed in the sunlight persisted. The assumption was, judging by the work of previous investigators, that at a sufficient degree of warmth the melanophores would contract and the skin turn green. Since a contracting effect was expected the experiments were of course conducted in the direct

sunlight. Each strip of skin experimented upon was placed in a vial as previously described and the physiological salt solution in which it was immersed was heated by placing the vial in warm water. This heating process was continued until the temperature of the salt solution had risen to a point high enough to produce a reaction of the melanophores.

Observations were made upon four separate pieces of skin all of which were dark brown in the direct sunlight at 30°C. at the beginning of the experiments. This color was maintained in all cases until at least 40°C. At this point, however, one of the pieces changed its color from brown to green. Of the other three pieces, one turned green at 43°C., and the other two at 44°C. and 47°C., respectively. In accordance with what we know of the mechanism of such color changes, this assumption of a green color can be taken as clear proof of a contraction of the melanophores. It can, therefore, be said that below an average of about 43°C. the behavior of the melanophores of excised pieces of Anolis equestris skin is not determined by the temperature of the environment. The time required to raise the temperature from 30°C., the approximate temperature of the physiological salt solution when the skin was first immersed in it, to a point sufficient to produce this contraction of the melanophores in the direct sunlight was from three to four minutes. That the contraction of the melanophores was maximal seems obvious, since in all cases the green color so produced was as brilliant as that associated with the green color assumed in the shade. Furthermore, these color changes in the strips of excised skin were not due to any killing of the pigment cells by excessive warmth, for if the temperature was lowered, thus permitting the action of light to reassert itself, the pieces of skin once more assumed a dark brown color.

Having shown then that the color of excised Anolis equestris skin is determined by illumination up to an average of 43°C., the next step was to determine at how low a temperature the same factor is capable of governing the responses of the melanophores. Since cold was expected to have an expanding effect, all of the experiments concerned with low temperatures were conducted in the shade, for an expansion could, of course, manifest itself only under such conditions of illumination. The cooling of the physiological salt solution was accomplished by immersing the vial containing the strips of skin in ice water. Experiments were performed upon three pieces of skin, all of which maintained a green color until the temperature had at least fallen to 9°C. At this point, one strip of skin changed from green to brown, while of the other two strips, one turned brown at 8°C., and the other at 6°C. The assumption of the brown color by the pieces of skin was, of course, indicative of an expansion of their melanophores. On the average, then, it may be said that the melanophores of isolated pieces of Anolis equestris skin expand at 8°C.

regardless of the illumination. The time necessary to cool the skin from 30°C. to a point low enough to produce this effect was about five minutes. As in the case of the responses to warmth, the excessive temperature did not kill the pigment cells, since raising the temperature again lead to a contraction of the melanophores.

The foregoing results show that between an average of 8°C. and 43°C. the behavior of the melanophores of excised Anolis equestris skin is determined by illumination. However, under certain circumstances an exception must be noted to this statement. Observations showed that melanophores previously expanded in the shade by cold, and subsequently subjected to a higher temperature of 35°C. or above when again stimulated with low temperatures, turned brown in the shade at approximately 18°C. The procedure in a typical case of this kind was as follows, the whole experiment being conducted in the shade. First, the melanophores of an isolated strip of skin were expanded by exposing them to a temperature of 6°C., following which they were immediately contracted by raising the temperature to 45°C., this operation requiring about three minutes. However, on once more lowering the temperature of the physiological salt solution, the melanophores instead of remaining contracted until 6°C. was arrived at, suddenly expanded at 20°C., a point reached in about two minutes after the cooling had begun. In four experiments of this sort, the skin having been previously heated to any point betwen 35°C. and 45°C., the melanophores expanded at temperatures of 17°C., 22°C., 20°C. and 11°C., respectively. These figures yield an average of 17.5°C., a point considerably higher than the one already given as the lowest temperature at which the responses of the melanophores are no longer governed by illumination. Therefore, it seems certain that the previous exposure of the skin to warmth produced an alteration of the threshold of sensitivity to cold, an effect that permitted a considerably higher temperature to act as an expanding stimulus than was the case on the initial exposure to low temperature.

A variation from the reactions just described was observed in two pieces of skin. Both of these pieces at first reacted in the usual way, darkening at 8°C., and then turning green when the temperature was raised to 35°C., these responses as well as those observed later occurring in the shade. On lowering the temperature a second time, however, one piece again darkened at 10°C., and the other at 20°C., but on continuing this cooling process, the piece that had darkened at 10°C., unexpectedly turned green at 7°C., and the one that had darkened at 20°C. turned green at 10°C. Warming this last strip of skin a second time, and then once more lowering the temperature lead to an expansion of the melanophores at 10°C., an expansion that proved to be permanent for the condition of the cells was unaltered at 5°C. It is difficult to say what the

explanation is for this unexpected contraction of the melanophores at low temperatures. Whether it was of common occurrence I was unable to determine, though repeating the experiment on two other pieces of skin under similar conditions failed to produce the response.

But no matter how we may attempt to account for the reactions just described, we are still justified in holding to the view that previous exposure of the melanophores to high temperatures does raise the critical temperature at which these cells expand in the cold. If then the responses to low temperatures are so influenced, what would be the effect of a previous exposure to cold upon the threshold of sensitivity to warmth? With the purpose in view of answering this question, a series of experiments was performed upon four different strips of skin. All of the experiments were conducted in the direct sunlight. Each one of the strips was separately subjected to 10°C., and then exposed to a rapidly rising temperature. In three out of four cases these excised pieces of skin showed no contraction of their melanophores until the temperature was well above 40°C., one of the pieces turning green at 42.5°C., another at 43°C., and still another at 45°C. There was one strip of skin, however, which did turn green at 37°C., but even when this figure is taken with the others the average temperature at which melanophores contracted after a previous exposure to cold was found to be 42°C., a difference of only one degree from the average critical temperature producing a contraction of the melanophores when the skin was first immersed directly in warm water. This difference hardly seems sufficient to justify the assumption that the threshold of sensitivity to warmth is altered by a previous exposure of the melanophores to cold. Further substantiation of this statement is given by the fact that after the contraction of the melanophores at 42°C., or above, a slight lowering of the temperature immediately produced an expansion. Therefore, by varying the temperature only a degree or so above or below the critical point of initial contraction, the color of the skin could be changed at will from green to brown or the reverse.

Discussion.—According to Parker and Starratt (1904) the color of Anolis carolinensis is determined between 10°C. and 40°C. by illumination, but above and below these points the controlling factor is temperature, the melanophores being contracted by warmth and expanded by cold. Parker (1906) demonstrated the same situation in Phrynosoma blainvillei except that the range within which illumination was effective was between 15°C. and 32°C. This was corroborated later by Redfield, who, working with the same species, roughly defines this range as being from 20°C. to 30°C. Since these data were all compiled from experiments performed upon whole animals at a time when their pigmentary effector systems were still under the control of the coördinative systems of the body, it is of interest to compare such data with the figures obtained from a study of the direct

effect of temperature upon the melanophores of Anolis equestris. In this species we have noted the range in which illumination is effective to be from 8°C. to 43°C., the lower point being subject to variation depending on the previous treatment of the pigment cells. The range for this species is then in close correspondence to that of Anolis carolinensis, and it is perhaps significant that the respective sensitivities to variations in temperature in Anolis carolinensis and Anolis equestris more nearly resemble each other than either one of them resembles the sensitivity to variation in temperature on the part of the melanophores of the horned toad, Phrynosoma blainvillei.

Redfield (1918) made further observations on the melanophores of Phrynosoma, and came to the conclusion that such stimuli act upon the pigment cells locally. He noted that local exclusion of light and local application of heat produced a localized contraction, though the local application of cold produced no expansion, but did maintain an expansion already established. Further experimentation indicated that the temperature reactions of the melanophores did not involve the action of any coordinating system. This statement he based upon the results obtained with the use of the method I have already described, these results being dependent upon the production of a localized contraction of the melanophores of horned toads when stimulated with warmth in regions where the skin had been operated upon in such a fashion that it was impossible for the responses to be governed by a nervous reflex. Since such stimuli were capable of calling forth the desired reactions his assumption seems justifiable.

Having found an independent reaction of the melanophores to temperature changes, Redfield was inclined to believe that such stimuli under any circumstances always affected the melanophores of reptiles directly. However, in a recent paper Hogben and Mirvash (1928) state that "exposure to a source of warmth in chameleons in which the cord and chain have been cut at, say, the fourteenth vertebra resulted in complete pallor anterior to the point of section only," from which they conclude that the temperature reactions of the melanophores of chameleon are influenced by the nervous system. Such being the case, it seems difficult to reconcile these two diametrically opposed results, unless one is to assume the chameleons to have a mechanism of melanophore control fundamentally different from that found in Phyrnosoma. Among the fishes it has been shown (Smith, 1928) that the behavior of the melanophores with respect to changes of temperature, presents two different aspects depending on whether or not the cells are innervated. Innervated melanophores on the trunk of Fundulus heteroclitus responded to high temperature by expansion, and to low temperature by contraction, while the same melanophores when denervated contracted at high temperatures and expanded

at low. Among the reptiles, therefore, the temperature reactions of the pigment cells, while under the control of whatever coördinating system may possibly govern their behavior, are identical with those of the denervated rather than the innervated melanophores of fishes. If then we may assume that the mechanism of response to temperature changes is the same in the pigment cells of the fishes and reptiles, a possibility as yet unproved, it would appear reasonable to say that in the reptiles the temperature responses of the melanophores are independent of any coördinating system, and are, therefore, direct. Although such a position is not without supporting evidence as we have seen, nevertheless it would be premature at the present time to make any sweeping assertions; the question, in view of the work of Hogben and Mirvash, being best held open until further experimentation has been done upon the reptiles.

The raising of the critical temperature at which the melanophores of excised pieces of Anolis equestris skin expand in the cold by first exposing the cells to warmth is comparable to similar observations made on the melanophores of fishes. In Fundulus (Smith, 1928) the denervated melanophores of the tail will expand from the stellate condition only when immersed in water at 5°C., or below, unless they are first immersed in water at 32°C., when they will expand at 20°C. But if instead of first immersing the tail in warm water where the cells contract at 32°C., it is placed in cold water and then immersed in water at higher temperatures it still requires the same degree of warmth, 32°C. to produce the punctate condition as it did before. In this instance the melanophores of fishes and reptiles again agree in their behavior, since in the skin of Anolis equestris it was impossible to alter the threshold of sensitivity to warmth, although such could readily be done in respect to cold. As these responses in both cases are due to the direct effect of the stimulus upon the cells, it seems probable that the melanophores of these two groups are alike in their independent reactions to changes of temperature.

Summary.—1. Between 8°C. and 43°C. the behavior of the melanophores of isolated pieces of Anolis equestris skin is determined by the conditions of illumination.

2. Above 43°C. the melanophores of such preparations respond directly to warmth by contracting, this response occurring independently of the illumination.

3. Below 8°C. the melanophores of such preparations respond directly to cold by expanding, providing they have not been previously subjected to high temperatures, this response occurring independently of the illumination.

4. Exposing the melanophores of an isolated piece of Anolis equestris skin to high temperatures will shift the critical temperature at which the melanophores expand in the cold from 8°C. to 18°C.

5. It is not possible to shift the critical temperature at which the melanophores expand in the warmth by any previous exposure of the cells to cold.

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FURTHER STUDIES ON THE INFLUENCE OF A POWER DAM IN MODIFYING CONDITIONS AFFECTING THE MIGRATION OF THE SALMON[1]

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In a paper presented last year[2] I embraced the results of some years' study on the conditions that control the movements of the sockeye salmon in freshwater during the period of the upstream migration when it is seeking the spawning grounds of its species. I pointed out that the streams of the Pacific coast which are utilized by the salmon for migration routes are also peculiarly adapted to utilization for power purposes and that this produced serious complications which could only be solved by intensive study of the habits of the fish. Observations were then reported to show that the sockeye in its upstream migration is definitely and primarily influenced by two physical factors: namely, the direction of the stream flow and the temperature of the water. The former influence determines the constant effort of the fish to pursue its course upstream. The temperature of the water serves to determine the choice of the fish at stream junctions where the sockeye selects definitely the stream having the lower temperature, and in the selection of spawning areas.

It was pointed out then that the installation of power dams modified natural conditions so distinctly and so considerably in respect both to stream flow and to water temperature that the changes effected influenced

the movements of the fish and brought about radical modifications in their life cycle as previously carried out in that stream. Further studies this year have yielded additional evidence both with reference to these influences and to others suspected but not demonstrated previously. It is my desire to present here the data secured in this study.[3]

The effect of the temperature stimulus was particularly noticeable at the power house where the discharge from the turbines formed a stream distinctly colder than the normal flow of the river, so that at the point where the discharge joined the remnant of the original stream the salmon were led to enter the tail race and fight the fierce current there in a vain effort to make their way up stream. These observations were confirmed this year and additional evidence was secured in that the fish later carried definite marks of the struggle in the form of abrasions of the skin and other bodily injuries produced by violent contact with definite areas such as portions of the concrete wall and the margins of the draft tubes. When worn out and injured the fish fell back and after resting endeavored to find another route for making the ascent of the stream. They were then too lacking in vigor to make the ascent of the fish ladder. Consequently, it appears clear that installations provided to assist the fish in surmounting such an obstruction in the stream must be placed where the fish can be diverted below the entrance to the tail race. Furthermore, to avoid the complications due to the mixing of waters different in temperature the point chosen for diverting the fish into a trap should be sufficiently far downstream that if waters of different temperature have been mixed the stabilization of the stream has been re-attained.

A very definite direct effect of the temperature stimulus was shown by observations at Sulphur Creek, one of the small tributaries of the Baker River which empties into that stream just above the head of the artificial reservoir, Lake Shannon, created by the construction of the dam. Sulphur Creek originally carried water sufficiently impregnated to be noticeable and when I studied the river some years ago it did not attract the migrating salmon. Since that time the upper waters of the creek have been entirely diverted for power purposes and the present discharge comes from several large springs only half a mile above the mouth of the stream. The water is of exceptional quality and lower in temperature than that of the Baker River into which it flows. This summer it was found that some sockeyes had left the river and were lying in pools near the mouth of this creek, having been diverted from the normal migration route apparently by the temperature of the water. The volume of the creek is so small in comparison with that of the river that evidently only those fish which chanced to move up river close to the discharge of the creek water would come under the influence of the lower temperature and be attracted into Sulphur Creek.

The definiteness of the response to the stream influence was well illustrated by another experiment tried this year. Some fifty fish which had been lifted over the dam were towed in a crate about four miles to the point in the lake known as "the narrows" and after being tagged were thrown overboard. The fish naturally struck the water in all sorts of ways. As they started to swim they oriented themselves positively without a single exception in two ways: first, toward the mouth of the river which lay several miles beyond at the upper end of the narrow stretch, and second, toward the cooler water at the bottom of the lake.

As the fish struck the water each one swam definitely and without hesitation, turning clockwise and making in some cases a full half-circle or a little more in those instances where such a turn did not involve more than 240 degrees approximately. The turn brought them head on in line with the main channel. At the same time each one directed its course obliquely down so that after traveling 100 feet or more it was lost to sight in deeper water. The movement into deeper water was determined possibly by two factors, namely, the lower temperature of the water into which the fish moved and also the reduced illumination of that region. The sockeyes are not violently photophobic, although their movements are restricted if not entirely held up during the hours of the day when the water is most brilliantly illuminated by the rays of the sun. They are particularly active in the morning and afternoon hours and on days sufficiently cloudy to reduce distinctly the illumination of the water.

The number of fish captured and lifted over the dam was unfortunately small this year but of the number secured only a fraction has completed the migration route and reached Baker Lake in which this run normally spawns. In all 2110 sockeyes were put over the dam and up to October 11 only 901 had been captured at Baker Lake where the trap maintained across the outflowing river insures the capture of all sockeyes reaching that point. Last year 4158 sockeyes were put over the dam and 1328 were captured at Baker Lake. Since the condition of the fish was not good either year, part of the discrepancy may be explained by the physical condition of the fish, but this is hardly adequate to account for the large number that have disappeared between the two points. Evidence was sought but not secured that the salmon are definitely attracted to other spawning grounds except by the conditions found at Sulphur Creek and described above. It is known that cold springs exist below the surface level of Lake Shannon and with the drop in water level as the water is utilized for power purposes such areas may be brought into water sufficiently shallow to furnish conditions known at ordinary spawning grounds of the species. Indeed, one cannot say positively that the depth at any place would be sufficient to inhibit the spawning of the fish although so far as is known the species spawns in relatively shallow water. I have

outlined a program for the frequent periodical examination of certain areas with a view to secure evidence on this point. The murky, glacial waters of the Baker River preclude observations on conditions even a few inches below the surface of the stream and these conditions exist for some distance beyond the point at which the river water is discharged into the lake, but the water clears up between the head of the lake and the dam except where it is in places roiled by wash from the shores.

Observations at the fish ladder showed that the sockeyes were disinclined to enter even though conditions had been made easy. Their reluctance did not seem to be modified by changes in the volume, the depth of the water, or the temperature as experiments conducted at different times with modification of each of these factors did not materially affect the results. Again and again it was observed that the fish nosing along the barrier would recognize the entrance to the trap and even test the water there by poking the head into the opening only to withdraw and proceed to search further, definitely rejecting the opportunity offered. Furthermore after being attracted to the first pools of the ladder they spent much time nosing along the sides of the boxes, even lifting themselves out of the water as they tested apparently the character of the barrier from point to point. They also jumped along the sides much more frequently than they did at the inflow into the pool from the higher level and made further not infrequent efforts to escape at the point of outflow from the pool where the entrance was trapped to prevent the fish returning down stream. All of these activities seem to show distinctly that the fish were dissatisfied with the conditions into which they had been brought so definitely as to seek to escape down stream rather than to continue the normal movement up stream against the current. The most probable explanation of this reversal of the ordinary response appears to be the quality of the water. At some other points I have observed previously that the salmon will not enter streams which carry water of uncertain quality. This has been definitely referred to in the description of conditions some years ago at Sulphur Creek. The very highly developed olfactory organs of fish and experimental evidence of other studies on the reactions of fish suggest that the conduct of the sockeyes here was conditioned by the quality of the water. Two factors may be suggested as possibly having modified the quality of the water in this case. Extensive alterations had been carried out in the form, depth and volume of the pools of the ladder. These changes were effected by wood construction. The entire environment at the entrance to the ladder was of fresh sawn, rough lumber. This may have affected the water. Again the fish which remained even a short time in the pools of the ladder became very badly fungused and thereafter made no effort to advance further, choosing rather to lie almost motionless resting in the

water. However, in swimming or floating around the pool listlessly they came in frequent contact with the walls which were thus smeared with contaminated mucus from the surface of the fish. It is not unlikely under these circumstances that the polluted water would repel those sockeyes which were testing in the fashion already described the quality of the stream emerging from the ladder.

Brief reference was made in the previous paper to the down-stream movement of the young sockeyes. These fish, which are known as migrators, start down stream from the lake in which they spend their first year in the late winter or early spring following the year in which they were hatched. Observations at Baker Lake and in Baker River have not been sufficiently definite to justify making an absolute statement as to dates and other details of the movement there. However, this part of the migration has been carefully watched at some other places and probably conditions do not vary greatly in general here. Elsewhere the young fish gather near the mouth of the lake and start down stream at a rather definite time. Here, after the trip down stream from Baker Lake, they have been observed moving along the shores of the artificial reservoir, Lake Shannon, and accumulating near the dam in large numbers. When the gates are opened these fish go out with the water and down the stream further. No evidence has yet been secured to show what part of the group makes successfully the drop down the surface of the dam and the passage through the turbulent waters at its base.

But it is doubtful if all the migrators attempt to leave Lake Shannon in this manner. What comes of those which do not? In my previous paper I wrote as follows:

"It is certainly true that large numbers of what are probably red salmon remain in the lake and after the surface waters warm up, seek the deeper spots. They apparently retire below the thermocline when it is formed and spend the summer in the deeper waters. There is no evidence to show whether they return to the surface after the fall overturn and continue their downstream migration or whether by virtue of the stop in their oceanward migration, they become a landlocked variety."

Last year a few small strange fish were caught spawning on the sockeye spawning grounds at Baker Lake. These fish were apparently dwarf sockeyes and a few eggs which were secured, fertilized and hatched, gave rise to typical sockeye fry. The discovery did not lead to any particular comment then and was not called to my attention. This year a considerable number of similar fish were captured about the end of August. They are a dwarf variety of the sockeye and correspond closely to the landlocked variety of the species as known at other points. Since the fish are too small to be caught in the net at the outlet of Baker Lake and were only taken by chance it is impossible to form any accurate idea of the

number involved but the number that appeared this year was very much larger than was seen last year. One can hardly doubt that there has been established a race of sockeyes that is physiologically landlocked. Some of the migrators which went downstream were evidently led in Lake Shannon to abandon the shore water along which the group was moving and to seek the deeper water. Possibly they represent the earliest arrivals which in the lapse of time lost the impulse to move downstream owing to the absence of a current in the lake and to their continuance in water that was current free. It should be noted that these are just the conditions which confront the migrators on emerging from the river into the sea. At that time the next move of the young fish is to seek deeper water. If through artificial interference with the current stimulus that is afforded by the stay in Lake Shannon, any migrator is led to carry out the impulse that succeeds next in the normal life history, such a fish would naturally move into the deeper water of the lake.

It may be also that the warming up of surface water in the lake due to the rising temperature as spring advances, establishes unfavorable conditions and further influences some of the migrators to seek deeper water. Another factor in the situation may be the gradually increasing amount of effective illumination of the water which comes with the lengthening of the days and the more nearly vertical rays of the sun. Whatever the factor or factors involved it is clear that once the young fish have moved into the darker, cooler depths of the lake they are physiologically imprisoned. They will not be acted upon by environmental conditions which impel them to migrate further but will remain in this region until growth and the approach of reproductive activities stimulate them to a new course of action.

It was noted this summer that with the warming of the surface waters in Lake Shannon the fishermen reported that fishing was poor. All the young fish had left the surface and those caught at later periods were all taken from water below the warm surface stratum. The conditions in this stratum this year were identical with those reported last year. During August the surface water reached the temperature of 68 and even 70°F. This warm surface stratum was not thick and the cooler water occurred at a depth of 12 to 15 feet.

The landlocked variety of the sockeye as known at other points is greatly inferior in size and weight to the normal race and these conditions would naturally be accentuated in a new body of water like Lake Shannon where the supply of food must be scanty at best. These fish ripen at an early age and moved by the reproductive stimulus would migrate upstream, reaching thus naturally the spawning grounds in Baker Lake. This part of the run would be of no commercial value and would contribute to the support of the run in the stream only in a very indirect fashion. Since

the formation of the landlocked variety is due directly to the installation of a power dam, the condition just described presents evidently another difficulty in providing for the maintenance of the sockeye run in this stream. Under the best of circumstances a part of the run, and for all we know a considerable portion, has been cut out of that which reaches the ocean and participates in the part of the life cycle which is of commercial importance.

The double loss at the power dam, namely, in the adult fish which come up the river but do not reach the normal spawning grounds and in the young fish which come down the river but which never reach the ocean, increases so greatly the difficulties inherent in the situation that one is brought to inquire whether the problem of preserving this valuable natural resource cannot be handled in some other fashion. While the method of catching the adults and getting them over the dam can certainly be greatly improved, nevertheless it is difficult to see how the difficulties associated with the downstream movement of the migrators can be effectively surmounted. It might be possible to install below the dam facilities for capturing, holding, and spawning the adults and then hatching the eggs. Under these circumstances the double loss would be avoided. Hatchery methods are sufficiently developed to justify definite predictions with reference to the number of fry which can be secured under these conditions provided the factors of water supply, etc., are properly guarded. However, the studies of Gilbert on the scale markings of the salmon have demonstrated that no sockeye returns from the ocean to freshwater except those which give evidence of having passed one year in freshwater before entering the sea. Consequently if the method proposed above is to be adopted it must include the installation of proper breeding ponds and the feeding of the fry until they have reached the appropriate age for release into the river. I think it is not beyond the ability of the fish culturist to control these conditions on the basis of present knowledge and apparently the difficulties in the situation are far less than those which confront one seeking to solve the problem of power dams and salmon migration under any other conditions yet suggested.

[1] Contribution from the Zoölogical Laboratory of the University of Illionis, No. 336.

[2] Ward, Henry B., "The Influence of a Power Dam in Modifying Conditions Affecting the Migration of the Salmon," *Proc. Nat. Acad. Sci.*, **13**, 827–833, December, 1927.

[3] Research prosecuted under the auspices of the Department of Commerce, Bureau of Fisheries, Washington, D. C.

PHARMACOLOGICAL SYNERGISM OF STEREOISOMERS

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Introduction.—Synergism in pharmacology is the term applied to the phenomenon exhibited by the combination of two or more drugs in which the pharmacodynamic effect produced by the mixture is not a simple summation of the effects produced by the two or more individual components. Such combinations produce a pharmacological effect of an unexplained nature in that the effect of one of the components may be greatly heightened or *potentiated* by the other or in other cases an *antagonistic* action of one drug over the other may be shown. A well-known example is "twilight sleep," induced by a combined administration of morphin and scopolamin.[1] Such a combination induces a narcosis very much deeper than could be produced by even double doses of either component when given alone. Quite a number of other such striking examples of synergism are known to the pharmacologist. Among them may be mentioned the effect of combinations of adrenalin and cocain on blood vessels noted by Fröhlich and Loewi,[2] the potentiation in respect to raising of the blood pressure exhibited by combinations of nicotin and lobelin described by Storm Van Leeuwen and Lind Van Wyngaarden,[3] the remarkable analgesic synergism of opium alkaloids noted by Macht, Herman and Levy[4] first published in these PROCEEDINGS and the synergistic effect of opium alkaloid combinations on the respiratory center studied by Caesar,[5] Straub,[6] and Macht,[7] all of which are not only of a purely scientific interest but also have a most important therapeutic bearing. An intimate analysis of these curious synergistic effects has been developed by Storm Van Leeuwen[8] and Bürgi,[9] whose published papers should be read by all those interested in the subject.

All of the studies on pharmacological synergism, as far as the author is aware, have hitherto concerned themselves with combinations or mixtures of drugs either of an entirely different chemical nature or of drugs chemically related and yet not identical in their structure. No studies have been made with combinations of stereoisomers, that is, of chemical agents exactly identical in structure with the exception of their configuration in space. The present author undertook a study of a number of such combinations in connection with certain puzzling pharmacological phenomena, the explanation of which could in the present state of our knowledge be best made on some such hypothesis as a synergistic reaction of two stereoisomeric pharmacological agents.

Substances Studied.—Several sets of optic isomers were examined. While it was not possible in each case to obtain all the three varieties of each drug, namely, the levo, dextro and racemic forms, any two stereoisomers of each group were quite sufficient for the present purposes to answer the problem undertaken. The following chemicals or drugs were studied: L. nicotin and DL. nicotin, individually and in combination; L. epinephrin and synthetic or DL. epinephrin, individually and in combination; D. camphor and DL. or synthetic camphor, individually and in combination; L. hyoscyamin and DL. hyoscyamin (atropin) individually and in combination; L. hyoscin (scopolamin) and DL. hyoscin (scopolamin) individually and in combination; and the two pairs of optic isomers from the cinchona alkaloids, namely, quinin and quinidin, and cinchonin and cinchonidin.

These drugs were studied in respect to selected pharmacological and toxicological reactions produced by them on living animals or living plants and results obtained have been so clear-cut and important that they were deemed worthy of publication in a preliminary way in this place.

EXPERIMENTS OCTOBER 23, 1928. GOLD FISH (*carasseus aureus*) PLACED IN AQUEOUS SOLUTIONS OF NICOTIN (ALKALOID)

NICOTIN L. 1:1,000,000	NICOTIN DL. 1:1,000,000	NICOTIN L. PLUS DL. IN PROPORTIONS OF 1:3
4:08 Fish put in solution	4:08 Fish put in solution	4:08 Fish put in solution
4:21 Moribund, floating on side	4:26 Excitement	4:20 Moribund, floating on side
4:23 Death	4:33 Shallow breathing	4:22 Death
Killing time 15 min.	4:36 Floating on side	Killing time 14 min.
	4:40 Taken out and put in fresh water which is followed by recovery overnight	

Experiment October 31st, 1928, and November 1st, 1928. Three cats are kept under ether anesthesia and solutions of nicotin containing 0.05 milligram to 1 cc. are injected at the rate of 1 cc. per minute into femoral vein. Blood pressure tracings from the corotid artery were taken at the same time.

Cat (A) Injections of L. nicotin. Weight of cat 2.15 kilo. Total injected, 11 cc. equal to 0.55 milligram. Killing dose, 0.256 milligram per kilo. Killing time, 4.5 minutes.

Cat (B) Injections of DL. nicotin. Weight of cat 2.5 kilo. Total injected 20, cc. equal to 1.000 milligram. Killing dose, 0.400 milligram per kilo. Killing time, 7.5 minutes.

Cat (C) Injections of mixture of L. and DL. nicotin (equal parts). Weight of cat 2.4 kilo. Total injected, 11 cc. equal to 0.55 milligram. Killing dose, 0.229 milligram per kilo. Killing time, 4.5 minutes.

Experiments with Nicotin.—The effect of L. nicotin and DL. nicotin were studied on rats by intraperitoneal injections, on cats and rabbits by intravenous injections, and on goldfish placed in solutions of the alkaloids. It was found in all the experiments that the levo-rotatory nicotin was more toxic

than the racemic form. It was furthermore found that when the two varieties were mixed together the results obtained showed a definite synergism, that is, the toxic effect was greater than that which was to be expected from the simple *additive* effects of the two components. The following protocols will serve as illustrations.

Experiments with Epinephrin.—Natural or L. rotatory epinephrin (Parke, Davis and Company) and synthetic epinephrin (Flächer) were employed. Experiments were made on the effect of these alkaloids on the blood pressure of cats. It was found, as is already well known, that L. epinephrin was much more powerful in regard to its blood-pressure-raising properties than the synthetic variety. It was also found that a combination of the two varieties gave a marked synergistic effect, that is, the rise in blood pressure was greater than the mere additive action of the two components as is well illustrated by the subjoined curves.

(*a*) DL. Epinephrin 0.05 mg. gives rise of 9 mm. (*b*) L. Epinephrin 0.05 mg. gives rise of 60 mm. (*c*) L. plus DL. Epinephrin 0.025 mg. of each gives rise of 56 mm. (Synergism)

Cat 2.1 kilo. Ether October 30, 1928. Carotid blood pressure tracings.

Experiments with combinations of Epinephrines.

Experiments with Camphor.—The natural or D. camphor and synthetic or DL. camphor were employed. Zoöpharmacological experiments were performed on rats and the well-known epileptiform convulsions produced by camphorated oil injected intraperitoneally were studied in detail. In following the convulsive effects of camphor note was made as to the time of onset of convulsions, their frequency and violence, and their duration as well as the character and type. Furthermore, the time of

onset of collapse or prostration and the time of death were carefully marked down. It was found as a result of some two hundred experiments that when equivalent doses per weight of the animals were injected into the rats, the DL. camphor was definitely more potent. Convulsions came on more quickly and were more violent; the duration of each was longer; and collapse and death occurred sooner than in the animals injected with D. camphor. When mixtures of the two varieties were employed in proportion of 1:5 and even less the mixture proved to be more potent that the straight dextro-rotatory camphor. Although the experiments on convulsant action of camphor require a good deal of experience and careful observation, there was no doubt as to the difference noted above because tests were made with mixtures unknown to the experimentor and he was able to differentiate between pure D. camphor and camphorated oil to which some DL. camphor was added. The following protocol will serve as an illustration.

EXPERIMENT SEPTEMBER 18, 1928

A. Weight of rat, 70 grams. Injected 100 milligrams D. camphor in oil	B. Weight of rat, 70 grams. Injected D. camphor 80 milligrams plus 20 milligrams DL. camphor in oil
3:59 Injected	4:00 Injected
4:04 Mild spasm	4:01 Violent convulsions. Animal rolling over on its back
4:05 Convulsions and quivering of front legs	4:02 Violent convulsions
4:08 Convulsions	4:03 Lying exhausted
4:10 Quiet	4:04 Very violent clonic convulsions lasting 30 seconds
4:16 Violent convulsions	4:05 to 4:11. Very violent clonic convulsions shaking the cage, repeated every minute
4:20 Sitting up quietly	4:12 Complete collapse and exhaustion from repeated convulsions
4.30 Quiet	4:15 Moribund and trembling all over
4:30 No change	4:25 Death
4:40 Mild convulsions	
4:57 Convulsions	
5:13 Convulsions	
9:00 A.M. (next day) recovery	

Experiments on plant protoplasm were made with camphors on the growth of the roots of *lupinus albus* in normal nutrient (Shive)[10] solution and in the same nutrient solution containing small amounts of camphors dissolved in alcohol. Controls were made with corresponding quantities of alcohol. It was found by the methods employed by Macht and Livingston[11] and Macht and Lubin[12] that the DL. camphor was much more toxic than D. camphor for the growth of the plants, and that mixtures of

the two showed distinct synergism, in that they were *more toxic* than either of the components when used alone. The following protocol will illustrate.

EXPERIMENT ON GROWTH OF LUPINUS ALBUS. SOLUTION OF CAMPHOR 1:10,000

D. camphor	Growth compared with normal plants 62%
DL. camphor	Growth compared with normal plants 53%
D. plus DL. camphor (1:1)	Growth compared with normal plants 44%
D. plus DL. camphor (3:1)	Growth compared with normal plants 49%

Experiments with Hyoscyamins.—Levo hyoscyamin and the DL. form of hyoscyamin, more commonly known as atropin, were examined in the form of sulfates and hydrobromides. The experiments were made on cats' eyes in respect to their relative mydriatic powers. Exactly the same quantities of L. hyoscyamin and DL. hyoscyamin are introduced into the conjunctival sac of each eye of the same cat, respectively, and their mydriatic effect is noted especially after the maximum dilatation in each eye begins to wear off. In this way it was found in agreement with all previous investigators that the L. hyoscyamin was about twice as mydriatic in its effect as atropin. The author then proceeded to compare mixtures of the two varieties in different proportions. It was found that when a 1:1000 solution of atropin is instilled in one eye of a cat and a solution of atropin four parts and L. hyoscyamin one part (1:1000) is introduced into the other, the eye treated with the mixture exhibited a very much greater dilatation of the pupil. Even combinations of nine parts of atropin hydrobromide and one part of L. hyoscyamin hydrobromide were more mydriatic than the same concentrations of atropin alone.

Experiments with Hyoscins.—The hydrobromides of L. hyoscin (scopolamin) and DL. hyoscin were tested zoöpharmacologically on *cats*, and phytopharmacologically on seedlings of *lupinus albus*. Experiments on cats' eyes in respect to the mydriatic effect here also revealed that the levo variety was more powerful than the racemic one, and furthermore that combinations of the L. and DL. varieties in proportions of 1:4 and even 1:9 exhibited a synergism precisely like that found with hyoscyamins.

Experiments on the growth of the roots of *lupinus albus* in nutrient solution with and without the addition of the alkaloidal salts indicated that the L. hyoscin was more toxic for plant protoplasm than the DL. variety and the combination of the two gave a synergistic effect, as illustrated by the following protocol.

EXPERIMENT ON GROWTH OF LUPINUS ALBUS. SCOPOLAMIN HYDROBROMIDE 1:2000

L. hyoscin	Growth compared with normal plants 77%
DL. hyoscin	Growth compared with normal plants 81%
L. plus DL. hyoscin (2:3)	Growth compared with normal plants 66%

Experiments with Quinin and Quinidin.—Quinin and Quinidin are, ac-

cording to all chemical authorities, identical chemical substances with the exception of their configuration in space, quinin being levo-rotatory and quinidin dextro-rotatory. The sulfates and the hydrochlorides of the two alkaloids were examined. Experiments were made with intraperitoneal injections on rats, intravenous injection on cats, and on the growth of *lupinus albus* seedlings. Experiments on cats revealed that when a solution of quinin 1:1000 is injected intravenously into the femoral vein of a cat under light ether anesthesia at the rate of 4 milligrams per minute the killing dose of the alkaloid, with the standstill of the heart as the end point, was greater than the killing dose of a similar solution of quinidin; in other words quinidin was invariably found to be more toxic in such experiments. A *combination* of the two alkaloids was found to show a synergistic effect and was *more toxic* than either of the individual components. The following experiment will illustrate.

EXPERIMENT NO. 10. INTRAVENOUS INJECTIONS OF QUININ AND QUINIDIN IN CATS. ETHER ANESTHESIA.

Cat (A) Injected quinin hydrochloride 1:1000. Killing dose 66 milligrams per kilo.
Cat (B) Injected quinidin hydrochloride 1:1000. Killing dose 43 milligrams per kilo.
Cat (C) Injected quinin HCl plus quinidin HCl (1:1) 1:1000. Killing dose 42 milligrams per kilo.

A similar synergism was noted with intraperitoneal injections in rats.

Experiments on the growth of *lupinus albus* indicated that, unlike the experiments on the cats, quinin was more toxic than quinidin, as has already been described by the author elsewhere.[13] Furthermore, a combination of the two alkaloids exerted a synergistic effect of an *antagonistic* type, that is, the combination was less poisonous for the plants than either of the components taken by itself. The following protocol is an illustration.

EXPERIMENT ON GROWTH OF LUPINUS ALBUS. QUININ AND QUINIDIN HYDROCHLORIDES 1:1000

Quinin HCl	Growth compared with normal plants 28%
Quinidin HCl	Growth compared with normal plants 31%
Quinin plus Quinidin (1:2)	Growth compared with normal plants 32%

Experiments with Cinchonin and Cinchonidin.—These two alkaloids obtained from the cinchona bark are also isomeric, cinchonidin being the levo variety and cinchonin the dextro variety. The sulfates of these alkaloids were employed and tested for their killing power on cats and inhibitory effect on the growth of *lupinus albus*. Experiments on cats revealed that cinchonidin was more toxic than chinchonin and that the comparison of the two gave a synergistic effect as illustrated by the following protocols.

EXPERIMENT NO. 15. INTRAVENOUS INJECTIONS IN CATS. ETHER ANESTHESIA.

Cat (A) Injected Cinchonin Sulfate 1:1000. Killing dose 55 milligrams per kilo.
Cat (B) Injected Cinchonidin Sulfate 1:1000. Killing dose 40 milligrams per kilo.
Cat (C) Injected Cinchonin plus Cinchonidin (1:1) 1:1000. Killing dose 37 milligrams per kilo.

The effect on the growth of *lupinus albus* seedlings was as follows: Cinchonidin or the levo variety was more toxic than cinchonin. Combination of the two alkaloidal salts revealed a synergism of a toxic character, the mixture being more toxic than either of the components. The following protocol is an illustration.

EXPERIMENT ON GROWTH OF LUPINUS ALBUS. CINCHONIN AND CINCHONIDIN 1:1000

Cinchonin Sulfate	Growth compared with normal plants 91%
Cinchonidin Sulfate	Growth compared with normal plants 69%
Cinchonin plus Cinchonidin (1:1)	Growth compared with normal plants 68%
Cinchonin plus Cinchonidin (1:3)	Growth compared with normal plants 67%
Cinchonin plus Cinchonidin (3:1)	Growth compared with normal plants 72%

Comments.—The possibility of synergistic physiological effects by two stereoisomers is so obvious that it is surprising no one has noted it before. The mechanism necessary for the production of such a phenomenon is not at all difficult to conceive. To use a very simple analogy, two hands or two feet may be identical in shape and symmetry, yet neither hand nor foot of one side would fit into the glove or shoe belonging to the other. So on the basis of the side-chain theory it is not at all improbable that an individual cell may possess receptor groups of a levo and dextro type and a mixture of two stereoisomers would thus have a double point of attack in place of a single one in case only one of the optic isomers was used.

This conception of synergism on the part of stereoisomers sheds light on certain puzzling observations made by previous writers. Thus Cushny,[14] who has done much pioneer work on the physiological and pharmacological effects of optic isomers, states that on comparing L. hyoscyamin with the racemic atropin he found the former twice as active as the latter. He, therefore, concluded that the dextro variety produced no appreciable physiological effect. Later when an opportunity presented itself to him for examining D. hyoscyamin he found that it did possess some physiological action. Had that investigator experimented with combinations of small doses of L. hyoscyamin together with large doses of atropin or D. hyoscyamin he would have found a synergistic effect. The same is true of Cushny's observations on the relative vaso-constrictor effect of L. epinephrin and synthetic epinephrin. Because he experimented only with L. epinephrin alone and the racemic variety alone he was led to the conclusion that the dextro variety was practically inactive. This, how-

ever, he found later to be incorrect. In fact, the relative potency on the blood pressure of the L. epinephrin as compared with the DL. epinephrin could not be at all explained as a mean average of the L. and D. variety.

The importance of the synergism here described by the present author is not altogether of a purely scientific interest. Bearing in mind the fact that a vast number of the organic chemical constituents of both plants and animals contain asymmetric carbon atoms and are, therefore, optically active, and bearing furthermore in mind that in the process of metabolism such compounds undergo various changes and some of them are probably racemized, the conception of stereoisomeric synergism may be useful in explaining various puzzling phenomena encountered not only by the pharmacologist but also by the physiologist, pathologist and biochemist investigating either animal or plant life. The author is examining some amino acids in this respect.

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